GRAND RIVER
MISA PILOT SITE STUDY

PART I: WATER QUALITY ASSESSMENT

Watershed Management Section
Ministry of the Environment

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7/224

EXECUTIVE SUMMARY

The Ministry of the Environment planned and carried out water quality surveys of the Grand River in the vicinity of the Waterloo Sewage Treatment Plant (STP) in 1986 and 1987. The objectives of the study were: 1) to develop site-specific effluent requirements based on receiving water impact, and 2) to develop and document acceptable receiving water based assessment techniques and procedures. This report presents the results and analysis of water quality samples collected from point source discharges and the receiving water.

Instream water quality samples were taken for over 200 parameters at 17 sampling stations on 36 sampling days over a two year period from March 1986 to June 1987. Information about the effluent quality of the Waterloo STP was obtained from the sampling components of two studies "The Fluctuations of Trace Contaminants in Municipal Sewage Treatment Plants" (OME 1989) and "MISA - Thirty Seven Municipal Water Pollution Control Plants - Pilot Monitoring Study" (OME 1988). The Water Survey of Canada and the Grand River Conservation Authority supplied hydrological data. The sampling survey was designed to elucidate possible major effects such as seasonal and diurnal trends, downstream and cross-stream spatial trends and precipitation events. The sampling results indicated that many of the parameters had a low frequency of detection or were not detected at all. This subset of parameters include all the organic contaminants as well as several of the trace metals. Eleven parameters were shown to have significantly higher concentrations downstream of the Waterloo STP outfall than in the background upstream of the outfall. They were sodium, chloride, fluoride, filtered residue, strontium, conductivity, zinc, hardness, potassium, magnesium and pH. Twenty-one organic parameters were detected of the total 126 organic parameters that were analysed. Lindane (BHC-gamma) was the most prevalent organic, parameter detected in the water column.

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Sampling results also indicated that, for the trace metal and conventional parameters, there was a low to moderate impact from the Waterloo STP on the Grand River water quality.

Neither seasonal or diurnal cycles in instream water quality were observed even though the STP showed a significant daily variation in discharge volume. Sampling was performed to specifically investigate water quality changes due to precipitation events however this effect was masked by sources of statistical error or 'noise'.

Two models were used in the Grand River Pilot Site Study. The first, a simple mass balance model predicts concentrations of contaminants when fully mixed in the receiver for certain design conditions. Secondly, a Monte Carlo model was formulated to account for the frequency of occurrence of certain conditions. Results from the simple mass balance model were analysed and highlighted the advantages of a probabalistic formulation such as the Monte Carlo model. The most detailed model that can be used within the constraints of the available data was the Monte Carlo simulation Model. The modelling results for the trace metals lead, zinc and copper showed that the Waterloo STP's contribution to the rate of non-compliance was relatively small. The median effluent concentration for phosphorus should be reduced from 1.027 mg/l to 0.0792 mg/l to ensure compliance with Ministry policies.

The probabalistic formulation of the Monte Carlo method when used to determine the effluent limits gives the required effluent concentrations in terms of a two parameter lognormal distribution. To maintain a specified rate of compliance the mean value of effluent concentration as well as the variance in these concentration must be determined. The consequence of this method is that there is a range of effluent distributions that will give the required compliance.

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1.0 INTRODUCTION

1.1 Overview of MISA Initiative

With the June 1986 release of the Ontario Ministry of the Environment's White Paper entitled "Municipal-Industrial Strategy for Abatement (MISA)", a comprehensive program has been underway to control water pollution at it's source.

The White Paper outlined the means whereby toxic metals and organic compounds would be controlled initially through a regulatory framework to enforce technology-based effluent standards. These pollution control requirements will be based upon implementation of Best Available Technology for treatment which is Economically Achievable (BATEA).

Development of these controls will be brought about through the promulgation of two regulations:

1. the Effluent Monitoring Regulation, requiring dischargers to identify and measure concentrations and amounts of toxics in the effluents; and

2. the Abatement or Limits Regulation, which will specify available concentrations, as well as amounts or loadings of toxic pollutants for each discharger.

These technology-based limits are to be complemented by water quality-based effluent limits on a site specific basis. These limits will consider the sensitive nature of some water bodies where a technology-based limit is not sufficient to protect the environment. In this case, the more stringent water quality-based limits will be established and used in place of the technology-based limits.

1.2 Development of Water Quality-Based Effluent Limits

In order to determine if the environment will be adequately protected by BAT(EA), the Ministry has undertaken a program to test and evaluate a number of traditional and novel water quality assessment techniques. These techniques have been applied on a site specific basis at six pilot sites throughout Ontario with a view to assessing their adequacy for establishing water quality-based limits.

The six pilot sites have been selected to provide a cross-section of industrial and municipal dischargers as well as a variety of receiving water environments which occur in Ontario. They are as follows:

Kaministiquia River at Thunder Bay	- Canadian Pacific Forest Products
St. Mary's River at Sault St. Marie	- Algoma Steel
St. Clair River at Sarnia	- Dow Chemical
Grand River at Waterloo	- Waterloo Sewage Treatment Plant
Lake Ontario at Toronto Treatment Plant	- Toronto Main Sewage
St. Lawrence River at Cornwall	- Municipal and Industrial Sources

As a basis for determining the impacts on the receiving environment, the pilot site study teams have relied on the Provincial Water Quality Objectives (PWQO's) and other biologically-based jurisdictional guidelines to determine acceptable conditions. Additional PWQO's/G's (Guidelines) for an expanded range of toxics were also developed in support of this program.

To establish the cause-effect links between source and receiver, these studies have built upon classical biological and modelling

assessment techniques to account for the intricate behavior and impact of some of these toxic compounds.

As a result, a number of innovative sampling, analytical and interpretive methods have been applied and subsequently evaluated for their utility in the overall mechanism of setting water quality-based effluent limits.

2.0 SITE DESCRIPTION

2.1 STUDY AREA

The Grand River watershed basin is the largest drainage basin in Southwestern Ontario (Chapman and Putnam, 1984). The total watershed drainage area comprises 6,969 km^2 and includes the Conestogo, Nith and Speed tributaries (see Figure 2.1). From the headwaters in the Village of Dundalk to the river mouth at Lake Erie, the Grand River spans 300 kms. Average annual flow at the mouth of the Grand River is 55 m^3/s with seasonal flows ranging from 6 m^3/s in the winter, to 1,800 m^3/s in the spring (GRIC, 1982).

Water consumption in the basin is primarily from ground water supplies, however 22 percent of domestic water is supplied from surface waters. Almost 90 percent of the municipal water demand occurs in the urban centres of Kitchener, Waterloo, Cambridge, Guelph and Brantford.

Other uses of the Grand River are recreation, ground water recharge, waste assimilation as well as supporting fisheries and associated wildlife.

The Grand River Pilot Site study area encompasses a 17 km stretch of the Grand River starting 500 m upstream of the confluence with Laurel Creek and extends south to the King Street East overpass at the Village of Freeport (Figure 2.2). The Waterloo Sewage Treatment Plant (STP) discharges it's effluent about 100 metres downstream of Laurel Creek. The study stretch lies to the east of Kitchener-Waterloo and in places defines the city limits. The most upstream sampling site is north of the city limits and the river extends in a net southerly direction ending south of city, nowhere being outside the urban influence of the city. This section of the river meanders such that 17 km of river length covers 8.5 km in straight line distance.

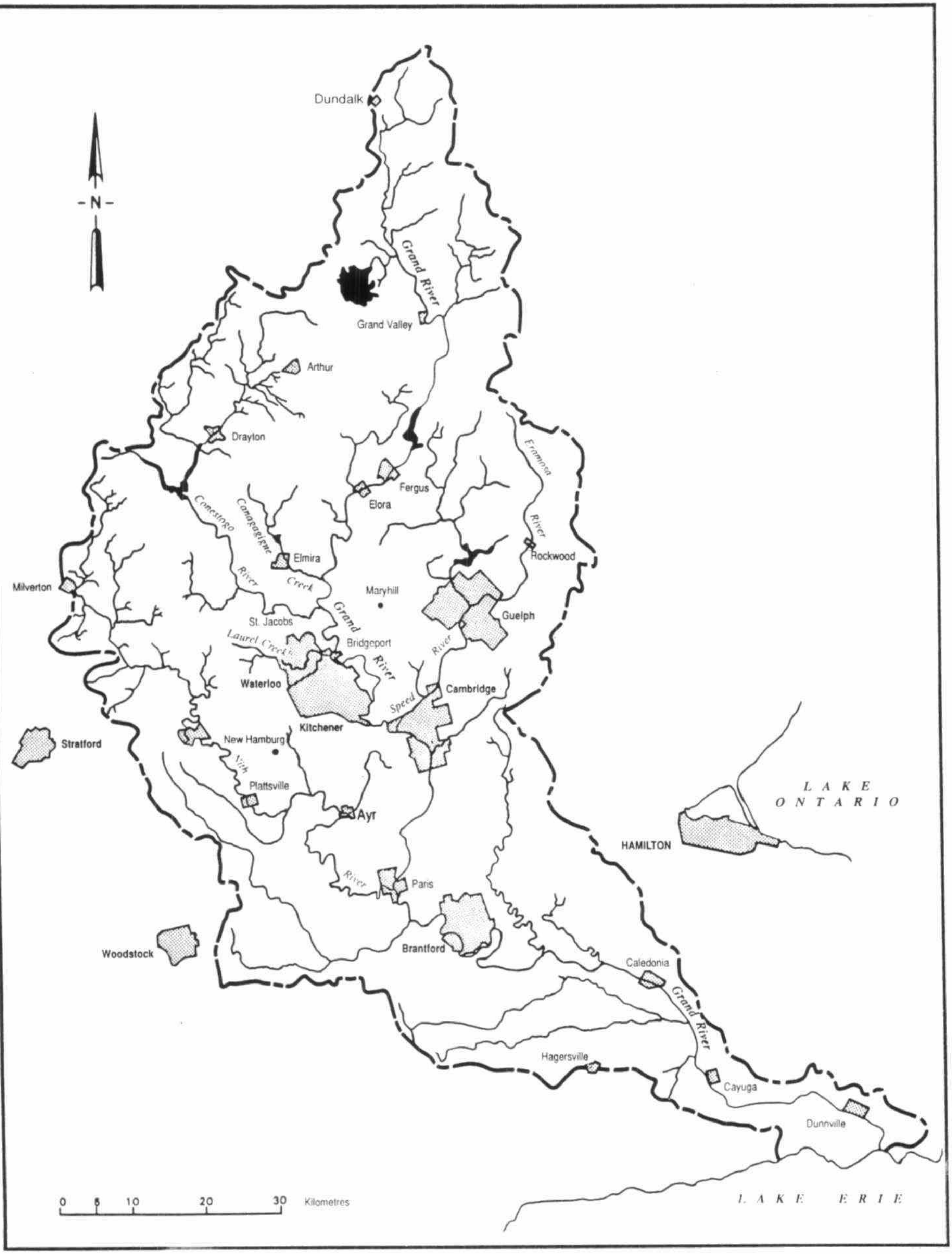


Figure 2.1: Grand River Watershed

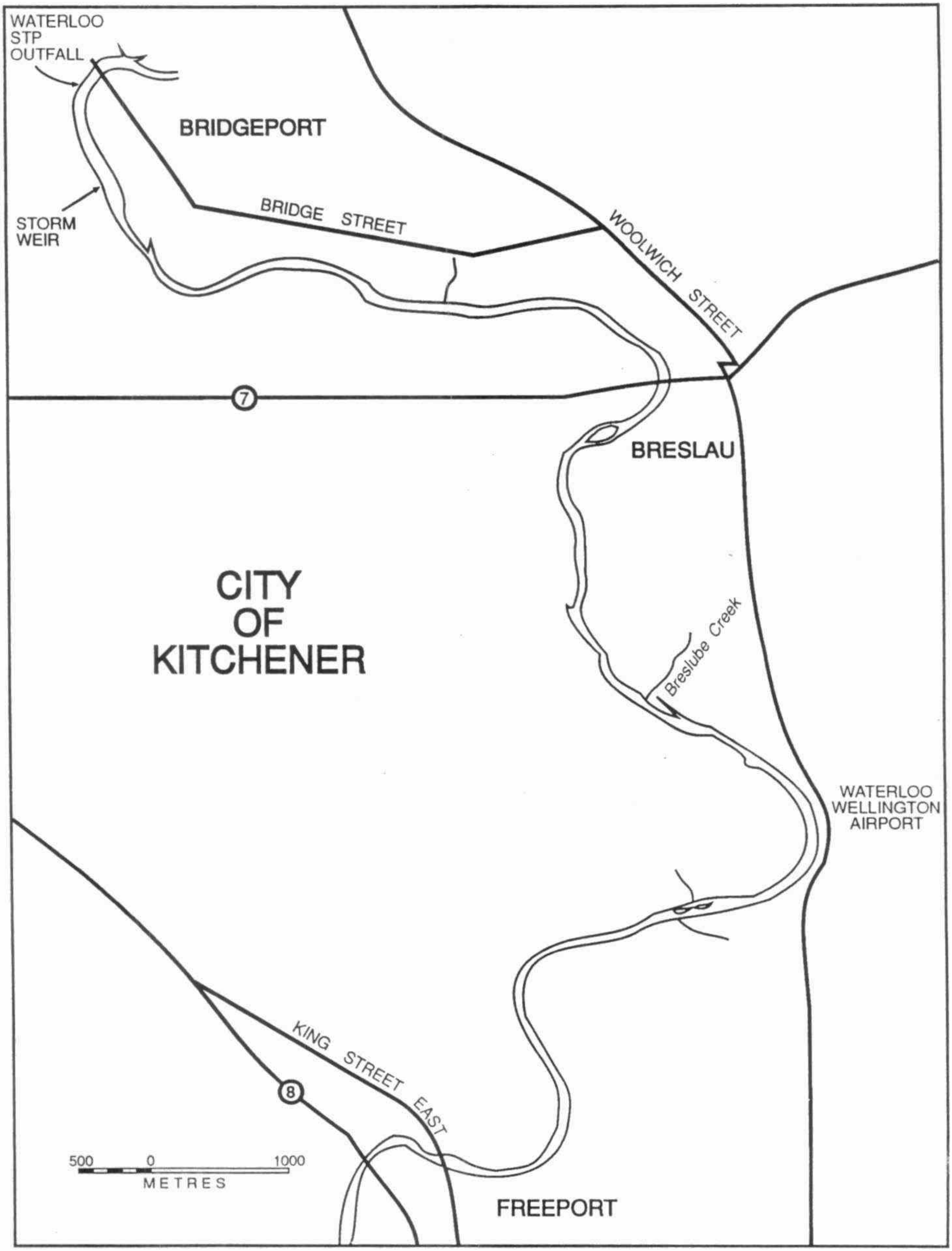


Figure 2.2: Map of Study Area

Land use within the basin is varied, with agricultural and rural land uses dominant in the northern and southern portions and urban land uses concentrated in the central portion. Agricultural and urban land uses comprise 70 per cent and 3 per cent of the basin area respectively. Wooded and/or idle areas account for approximately 19 per cent, while less than 1 per cent of the basin area lies in other uses. The bulk of the population resides in the cities of Kitchener, Waterloo, Cambridge, Guelph and Brantford (GRIC, 1982).

The topography within the central portion of the basin is rugged and hilly. It is characterized by kame and outwash sands and gravels, and extensive alluvial terraces adjacent to the Grand River. Surface soils are medium to coarsely textured and overlay a variety of well-drained tills, sands and gravel deposits. The porous surficial material provides an excellent system of ground water aquifers (GRIC, 1982).

2.2 Waterloo Sewage Treatment Plant

The Waterloo Sewage Treatment Plant (STP) is operated by the Ontario Ministry of the Environment and is a conventional activated sludge plant with continuous phosphorus removal. Municipal sewage treatment plants depend to a large extent on biological processes and are designed to remove conventional contaminants such as oxygen consuming wastes and suspended solids. The Waterloo STP consists of comminutors, raw sewage pumps, grit removal tanks, primary clarifiers, sludge digesters, aeration system, secondary clarifiers and a chlorination system. The final effluent receives chlorination prior to discharge to the outfall sewer. Effluent from the plant is discharged via a 2 km, 1200 mm diameter sewer to the Grand River south of Bridgeport Road. The outfall is partially submerged and is situated on the west bank of the river.

At the time of the survey, the Waterloo STP capacity was 45,460 m^3/day (0.526 m^3/s) with an approximate service population

of 66,600 persons. The influent to the plant consists of industrial, commercial, residential and unaccounted for sources with relative contributions of 13%, 11%, 25% and 51% respectively. The high percentage of flow unaccounted for was likely the result of infiltration to the sewers (Proctor & Redfern, 1986).

Effluent limits for STP discharges of conventional pollutants provide the required protection for provincial receiving waters and are set to regulate the discharge of these parameters. These requirements are typically based on technology limits and may be further modified based on the capacity of a waterbody to assimilate wastes. Procedures for developing effluent limits are outlined under Policy 3 of Surface Water Quality Management within the "Blue Book" (OME 1984). Biochemical oxygen demand (BOD), suspended solids and total phosphorus have traditionally been used as indicators of plant performance and effluent quality.

For the design capacity of 45,460 m^3/d, the effluent limits were:

BOD_5 (Biochemical Oxygen Demand measured over 5 days)	= 25 mg/L
Suspended Solids	= 25 mg/L
Total Phosphorus	= 1.0 mg/L

The average daily flow for the STP exceeded the design flow capacity in both 1986 and 1987. It was indicated by plant operations personnel that there is no by-passing of the influent to Laurel Creek. The STP design flow capacity is the average daily flow expected at the plant. Sewage treatment plants are generally designed with the capability to process peak flows. Peak flows are those flows that exceed the design capacity for short durations and are a result of peak water usage within the system.

Due to increasing urbanization within the Waterloo area, the Waterloo STP must expand. Approval to expand in a staged manner by the addition of modules of a given size has been obtained to

raise the current design capacity of 45,460 m^3/d (0.526 m^3/s) to an ultimate capacity of 72,700 m^3/d (0.841 m^3/s). The first stage in the expansion was recently completed (June 1989), yielding a design capacity of 54,600 m^3/d (0.631 m^3/s. The Waterloo STP effluent limits are listed in Table 2.1.

TABLE 2.1 Waterloo STP Effluent Limits - Current Design Capacity (54,600 m^3/d)

	Effluent Objective
BOD_5	15 mg/l
Suspended Solids	15 mg/l
Total Phosphorus	0.8 mg/l
Chlorine	0.5 mg/l
Fecal Coliforms	200 counts/100ml

TABLE 2.2 Waterloo STP Effluent Limits - Ultimate Design Capacity (72,700 m^3/d)

	Effluent Objective
BOD5	15 mg/l
Suspended Solids	15 mg/l
Total Phosphorus	0.6 mg/l
Total Ammonium Nitrogen	1.8 mg/l
Chlorine	0.5 mg/l
Fecal Coliforms	200 counts/100ml

The effluent limits listed in Table 2.1 will apply only until January 1, 1992 or when a capacity of 54,600 m^3/d is reached. For a design capacity of 72,700 m^3/d, the effluent limits listed in Table 2.2 will apply. The operational performance of the Waterloo Water Pollution Control Plant is discussed in section 3.2.

3.0 STUDY OUTLINE

The objectives in designing a water quality sampling survey are to be able to, representatively and accurately, describe existing water quality conditions, and to gather sufficient data for the evaluation of impacts of contaminant loads from major point sources. The survey should quantify major effects and variability of the dynamic and complex nature of instream contaminant levels. In the survey design, consideration must be given to the need for data to compliment the predictive modelling tools that will be used for impact assessment and the setting of effluent limits.

Water quality in rivers is affected by point sources (industrial and municipal discharges) and diffuse non-point sources (urban and agricultural runoff). The sources of variability are of the following types:

1. temporal variability: seasonal/diurnal;
2. spatial variability: downstream sources and sinks - cross-stream variability due to dispersion;
3. precipitation event variability: wet weather, dry weather, snow melt run off; and,
4. variability between parameters: differences in water quality due to parameter specific variability.

A sampling grid of primary and secondary stations was developed to adequately address the inputs from point and non-point sources and to optimize the allocation of resources for the study (see Figure 3.1). Primary stations were located along the main branch of the Grand River as well as at major point source inputs and were sampled during most surveys. Secondary stations were located at minor point source inputs and were sampled intermittently.

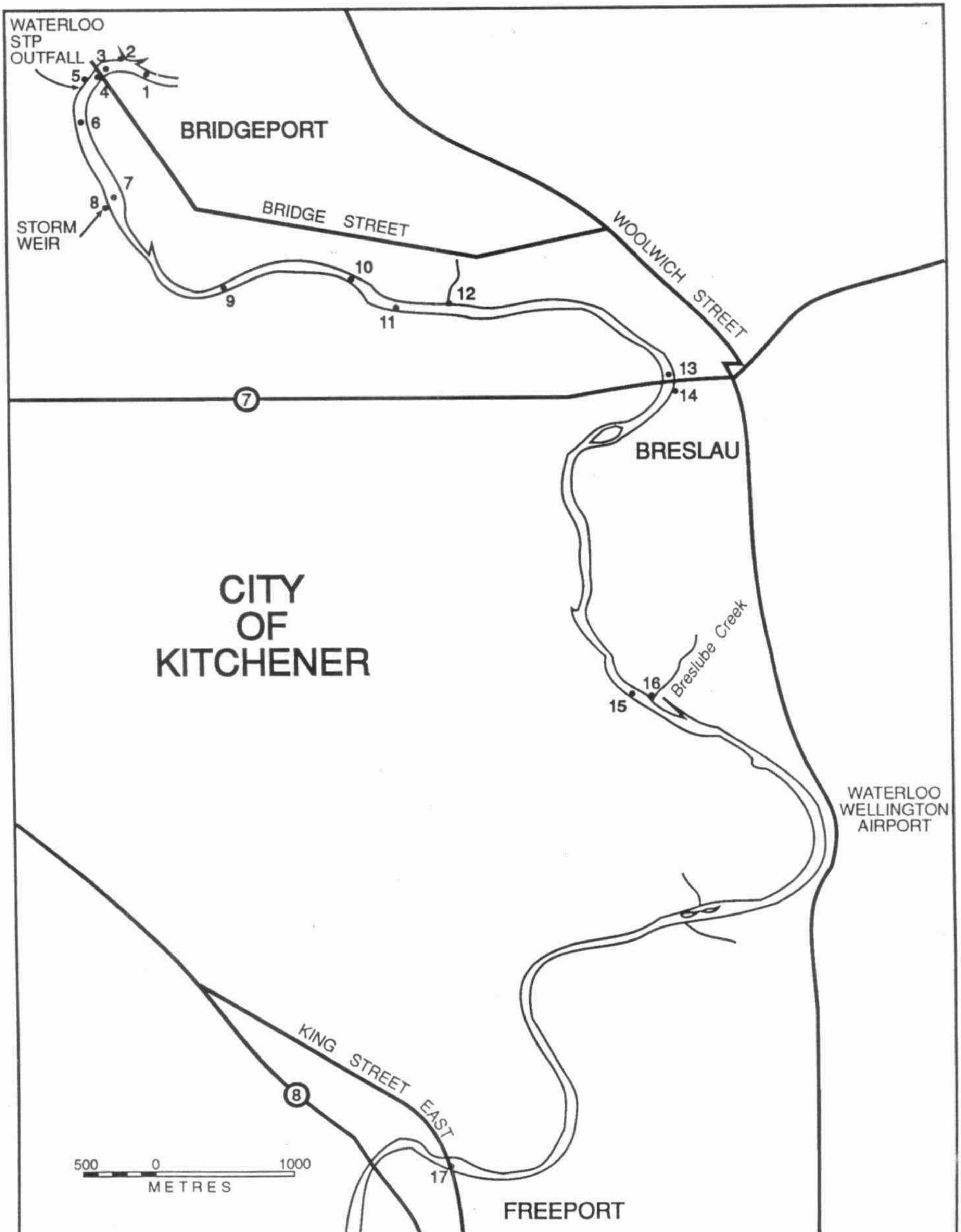


Figure 3.1: Study Area Sampling Locations

To assess effects of seasonal variability and derive estimates of average yearly water quality, sampling was undertaken on 36 different dates over a two year period from March 1986 to June 1987 (Table 3.1).

Two aspects of spatial variability; cross-stream and downstream, were considered. The downstream variations due to localized effects of point sources and the cumulative affects of diffuse loadings ~~was~~ were investigated by the placement of sampling stations. The sampling locations were chosen so that background conditions, with respect to the STP, could be compared to the downstream quality. To this end, sampling for the pilot site study was undertaken at seventeen locations starting with Station 1, 300 metres upstream of the Bridgeport bridge and extending downstream 17 kilometres to Station 17 at the Village of Freeport. Table 3.2 identifies these stations and describes their location with respect to the STP and the type of sampling undertaken.

3.1 Receiving Water Sampling

Table 3.1 is a detailed summary of the field sampling schedule for instream water quality, describing the dates, locations and types of sampling. Eight sample locations were sampled 20 times or more for dry weather intensive, dry weather monitoring, wet weather event and snowmelt runoff sampling. The remaining nine secondary stations were sampled on no more than two days. The sampling survey was designed to fulfill the data requirement for estimation of contaminant distribution values such as the mean and the degree of variablity. This timetable illustrates the method used to quantify temporal and precipitation effects.

Initial sampling was performed as a screening exercise. One aspect of a developed and partially urbanized watershed is the diversity of compounds in the environment as a result of the concentration of industries that use or produce chemical compounds. Screening

TABLE 3.1: SAMPLING SUMMARY

DATE	STATION NUMBER 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
86/03/14	4																
19	4																4
24	4																4
26	4																4
27	4																4
86/04/02	4																4
06	4																4
28																	4
86/05/06			1		2											2	
13	2	2			2			2					2	2	2	2	2
15			1														
86/06/05					2											2	
19	2	2			2			2					2		2	2	2
86/07/03	1	1			1								1			1	1
04	1	1			1			1					1			1	1
05	1	1			1			1					1			1	1
86/08/15	3	3			2			2					3		3	3	3
21			1														
26	3	3			3			3					3		3	3	3
27	3	3			3			3					3		3	3	3
86/09/10			2														2
86/10/24	2	2			2			2					2		2	2	2
86/11/27																1	
86/12/17	2	2			2			2					2		2	2	2
87/01/23	2	2			2			2					2		2	2	2
87/02/16			1														
87/02/02	5	5			5			5					5		5	5	5
03	5	5			5			5					5		5	5	5
04	5	5			5			5					5		5	5	5
05	5	5			5			5					5		5	5	5
06	5	5			5			5					5		5	5	5
07	5	5			5			5					5		5	5	5
87/05/21			1														
26	3	3			3			3					3				
87/06/16	2	2		2*	2	2*	2*	2	2*	2*	2*	2	2*				
17	2	2		2*	2	2*	2*	2	2*	2*	2*	2	2*				

* sampling on left side, right side & centre of river/ 1- dry weather intensive sampling/ 3 - wet weather sampling/ 4 - screening sampling/ 5 - snowmelt runoff sampling.

TABLE 3.2: __Sampling Site Description__

Station	Description	Distance Downstream from STP (metres)
1	GRAND RIVER above Bridgeport - upstream limit of survey area - characterization of background levels of all parameters	-886
2	LAUREL CREEK - major source of urban runoff - characterization of seasonal and flow related variations - wet weather and seasonal dry weather sampling	-337
3	GRAND RIVER at Bridgeport - dry weather monitoring - Grand River Conservation Authority streamflow gauge	-165
4	GRAND RIVER 10 m upstream of STP - dry weather monitoring	-10
5	WATERLOO STP - primary point source - samples taken from point of disharge	0
6	GRAND RIVER 600 m downstream of STP - dry weather monitoring	600
7	GRAND RIVER 10 m upstream of storm weir - dry weather monitoring	1015
8	TRIBUTARY #1 Storm Weir - characterization of urban non-point sources	1025
9	GRAND RIVER 2200 m downstream of STP - dry weather monitoring	2~~1~~200
10	GRAND RIVER 3000 m downstream of STP - dry weather monitoring	3000
11	GRAND RIVER 3500 m downstream of STP - dry weather monitoring	3500

TABLE 2.4 (CONT.)

Station Number	Station Description	Distance Downstream from STP (metres)
12	TRIBUTARY # 2 - dry weather monitoring	4185
13	GRAND RIVER at HIGHWAY # 7 - dry and wet weather sampling	6638
14	TRIBUTARY # 3 - dry weather monitoring	6688
15	GRAND RIVER above Breslube Creek - dry and wet weather monitoring	9690
16	TRIBUTARY #4 BRESLUBE CREEK - second major tributary - characterization of seasonal and weather related discharge variability	9808
17	GRAND RIVER at Freeport - downstream limit of survey area - characterization of integrated effects of point and non-point sources	16200

sampling, therefore, is an integral part of the rational of the MISA strategy. The Enhanced Monitoring Priority Pollutants List (EMPPL) was partially based upon a similar target group of organic parameters compiled by the USEPA and modified for use in Canada. The list of organic parameters analysed in the Grand River Pilot Site Study is a subset of the EMPPL. The remaining parameters were conventionals and metals. A complete list of the parameters is presented in Appendix A. Screening sampling was performed at station 1 and station 17, the upstream and downstream limits of the study area, for this large suite of contaminants to identify a smaller list of parameters for the other phases of sampling.

Twenty-four hour intensive sampling was carried out to assess diurnal variability. Dry weather low flow conditions may be the

most critical in terms of evaluating the impact of the Waterloo STP effluent on the river. In defining the most critical assessment condition, diurnal variation in both the effluent and the river are major considerations. To quantify this variability, grab samples were collected at four hour intervals over a 48 hour period from July 3rd to July 5th, 1986 at seven sampling stations.

During dry weather periods, changes in STP discharge rate and associated pollutant loads occur through infiltration, illegal industrial discharges, spills or changes in industrial loadings from shift changes or batch processing. In addition, variable river flows, agricultural practices, atmospheric loads and other seasonal effects may produce significant variations in ambient water quality. In an effort to investigate these effects, monthly samples were collected to assess the seasonal variability of contaminant inputs, predominantly from the upstream watershed.

Seven times over the sampling period of two years, 24 hour composite samples were taken. Composites consisted of grab samples taken at 4 hour intervals and physically composited. Analysis of these composites is therefore a representation of the average concentration over the 24 hour period. The composite samples were used to assess the variability of the average dry weather condition throughout the year.

Precipitation is a major cause of increased pollutant concentrations in surface waters. Snowmelt runoff is a similar mechanism for increased instream concentrations. The loadings are through point sources, such as storm sewers and tributaries as well as diffuse sources and airborne contaminants. Water quality and quantity conditions in a river are affected both by local weather events and events upstream in the watershed. To quantify these contributions wet weather surveys were carried out on four days during or after localized wet weather events. Snowmelt runoff effects were investigated by sampling over a six day period in April 1987 at the eight major sampling locations.

For a point source discharger into a limited receiver, defining the mixing zone of the effluent is an essential part of an impact assessment. A mixing zone is defined as an area of water contiguous to a point source where the water quality does not comply with the Provincial Water Quality Objectives (PWQO's). As a component of the Grand River Pilot Site Study a mixing zone study was conducted to quantify the cross-stream dispersion characteristics of the Waterloo STP effluent plume and make predictions about the area in the river that may be out of compliance with the PWQO's. Results of this study are discussed in the separate component report (OME, 1990).

3.2 Waterloo STP Effluent Sampling

As shown in Tables 3.1 and 3.2 sampling of the Waterloo STP was undertaken directly as part of this study. Due to the length of the discharge pipe (2 Km), sampling was performed as close as possible to the receiving water. Site limitations however, necessitated collecting samples in the effluent plume at the point of discharge. Sample results thus may have contained a small amount of the receiving water and would represent minimum amounts of contaminants contained in the effluent.

Two studies were conducted to investigate the operation of the Waterloo STP. The Waterloo STP was one of the plants studied in MISA program's investigation of thirty seven Ontario sewage treatment plants. A report entitled "Thirty Seven Municipal Water Pollution Control Plants - Pilot Monitoring Study" (OME, 1988) describes the results. A second study which included the Waterloo STP attempted to define the dynamic variation of effluent concentrations described in an unpublished report entitled "Fluctuations of Trace Contaminants in Municipal Sewage Treatment Plants" (OME, 1989).

The goal of the Pilot Monitoring Study was to provide information needed to support the development of cost-effective and practical

MISA Monitoring Regulations. The Waterloo STP was one of the thirty seven Ontario STPs selected for the Pilot Monitoring Study. Selection of this plant was based on the criteria that the average day flow in 1986 was greater than 45,000 m^3/d. A more detailed description of the selection criteria for the Pilot Monitoring Study may be found in the above noted report.

The field program for the Pilot Monitoring Study included the collection of composite samples of the influent and final effluent of the Waterloo STP for two periods of five consecutive days during the months of January and July 1987. These dates are considered representative of the "winter" and "summer" operating conditions at the STP. The samples were analyzed for conventional, organic and trace metal parameters.

The objective of the Fluctuations Study was to define the dynamic characteristics of effluents from full-scale STPs. The study investigated the response characteristics of conventional treatment facilities to typical input fluctuations in trace contaminants. The Waterloo STP was selected as one of the three full-scale Ontario STPs at which an intensive sampling program was conducted to quantify the degree of variability in the concentration of trace contaminants in the influent and effluent streams from such facilities. The Waterloo STP was selected to represent primarily domestic influent quality.

Intensive comparison sampling of the influent and effluent was conducted for a period of eight days from July 2 to July 10, 1986. This sampling consisted of grab samples of the influent and treated secondary effluent at two-hour intervals for approximately 200 hours; to provide an influent and effluent sequence of approximately 100 paired data points. The samples were analysed for conventional, organic and trace metal parameters.

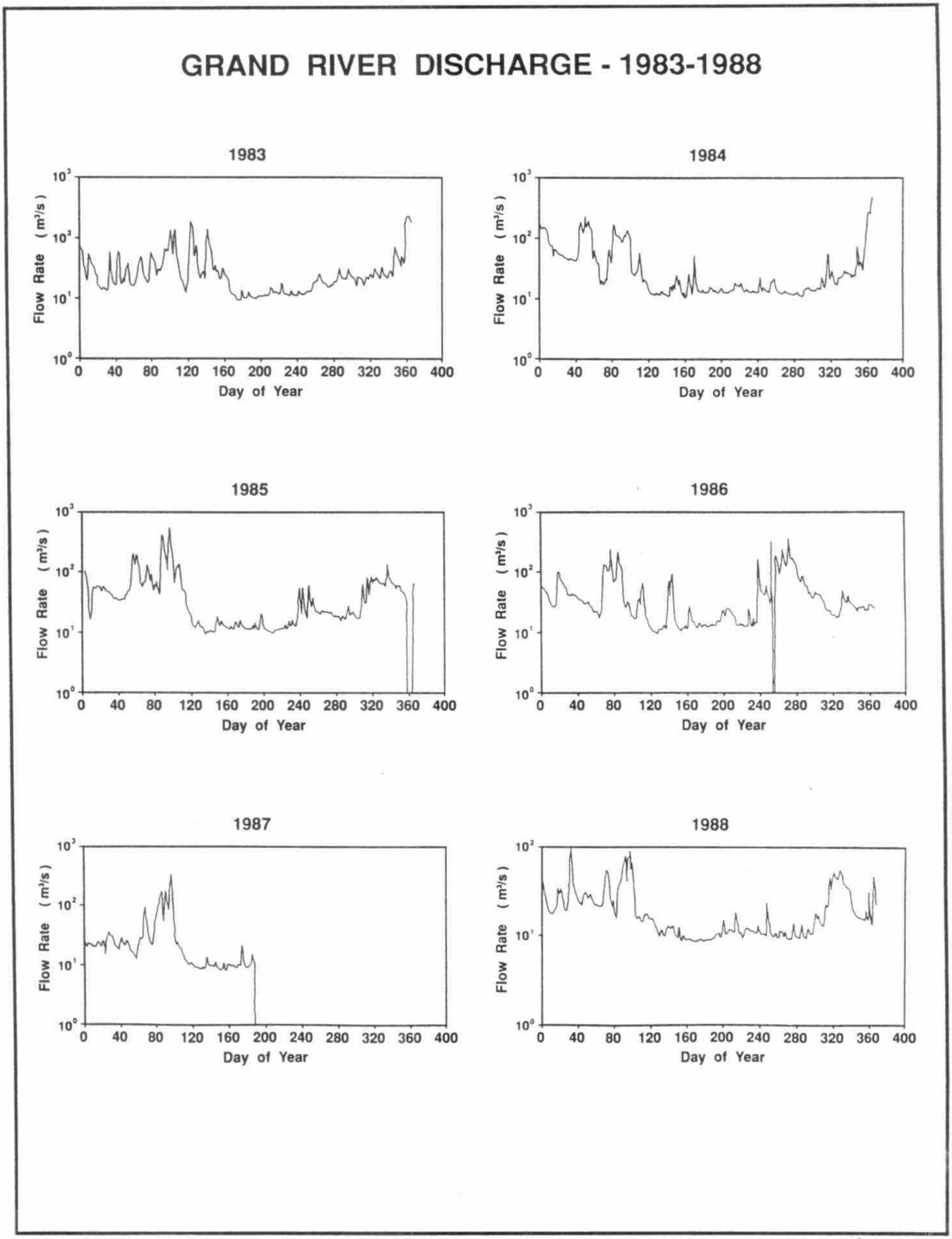


Figure 4.1: Time Series of Flows at Bridgeport Gauge

4.0 RESULTS

4.1 Grand River Hydrodynamics

An important element of water quality assessment in rivers is the volumetric discharge rate. A receiver, like the Grand River, is more sensitive to the impact of a point source contaminant discharge during periods of low flow and for this reason the magnitude of the low flow condition and it's frequency of occurence have been examined. The most commonly used low flow rate is the 7Q20. The 7Q20 is the lowest discharge rate that persists for seven consecutive days occuring on average once in twenty years. The Grand River Conservation Authority (GRCA) maintains a flow gauge at the Bridgeport Road bridge approximately 100 meters upstream of the Waterloo STP effluent outfall. Flow data from 1982 to the present were available as a direct measure of the background river flow rates for the study reach and federal gauging stations located at Grand River at West Montrose, Laurel Creek at Waterloo and Grand River at Galt were used for prorating discharges. The flow data time series from the Bridgeport gauge is presented in Figure 4.1.

The Grand River has a history of flooding during peak flows, and consequently flood controls have been implemented for the protection of life and property. Several dams have been constructed on the Grand River and it's tributaries upstream of the study area (GRIC, 1982) to regulate the flows. As well as protection from peak flows the dams operate to maintain a minimum low flow target of 8.4 m^3/s at the GRCA gauge at Bridgeport. Winter flows are not regulated and it is not known whether flows of less than the 8.4 m^3/s occur. Ice conditions which can effect flow gauges, yielding erroneous flow readings, are not corrected for at the GRCA gauge and therefore reliable estimates of winter low flows are not directly available for the study area.

A lognormal probability plot of the Bridgeport flow records is shown in Figure 4.2. This graph indicates that the median flow

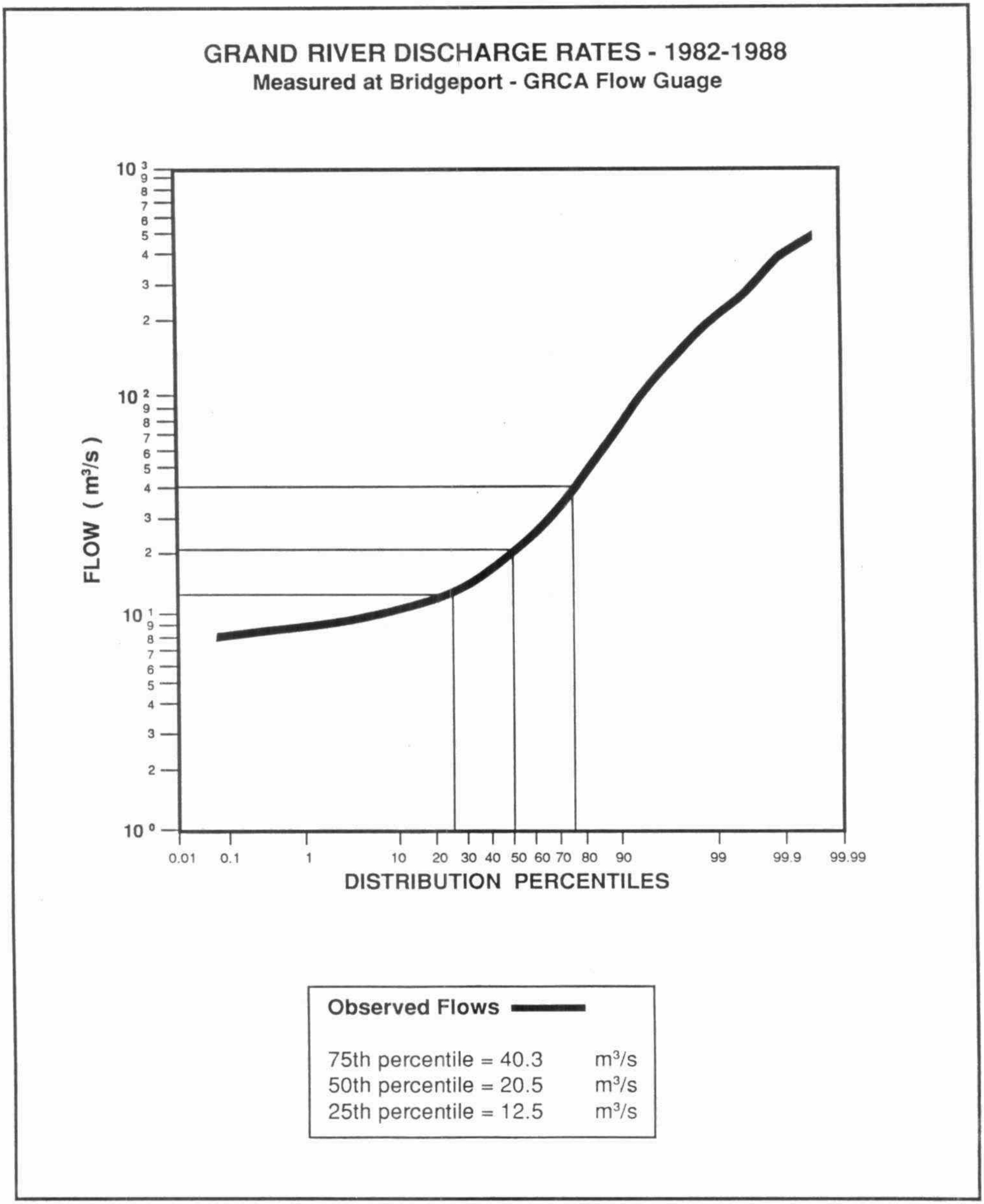


Figure 4.2: Lognormal Probability Plot of Bridgeport Flows

rate is 20.6 m^3/s and the upper and lower quartiles (75th and 25th percentiles) of the sample distribution are 40.3 m^3/s and 12.6 m^3/s respectively. The effect of low flow augmentation is apparent in the graph and indicates that the number of average daily flows less than 8.0 m^3/s is zero. An analysis of time-of-travel and average flow velocities was not required for the modelling in this component of The Grand River Pilot Site Study however, it was considered in detail in the mixing zone modelling component (OME, 1990).

4.2 Waterloo STP Effluent Characterization

Characteristics of influent and effluent from the Pilot Monitoring Study are presented in Table 4.1. Samples collected were analysed for 144 organic parameters and 15 trace metal and conventional parameters. Many of those parameters were not detected in either the raw wastewater or secondary effluent.

A summary of the influent and effluent characteristics for the Waterloo STP from the Fluctuations of Trace Contaminants Study is presented in Table 4.2. Table 4.2 summarizes estimates for the percentage removal of trace contaminants based on the study data. In addition, data presented in Table 4.3 illustrates the variability of the influent and effluent characteristics at the Waterloo STP. The variability of the parameters is expressed by the relative standard deviation (RSD) which was calculated as the standard deviation divided by the arithmetic mean. A low RSD percentage indicates a low variability.

It was reported in the study on Fluctuation of Trace Contaminants that municipal STP's were reasonably efficient in removing trace contaminants, and that treatment processes at the three sampled STP's significantly attenuated the variability exhibited in the raw influent. In general, effluent concentrations from the STP were less variable than influent concentrations for all categories of contaminants.

The study on Fluctuations of Trace Contaminants presented short term effluent fluctuation characteristics at the Waterloo STP. The resultant time series of effluent discharges to the Grand River was used for this study and is described in a subsequent section.

The Waterloo STP exhibited lower variability in effluent quality and generally lower parameter concentrations than the other STPs. In general STPs depend to a large extent on biological processes for the removal of oxygen consuming wastes, suspended solids and total phosphorus and thus are not very effective in the removal of organic contaminants. The removal of several trace metals occurs as a result of suspended solids removal, due to the affinity of the trace metals with the particulate matter.

4.3 Grand River Ambient Water Quality

In this section the results of the Grand River Pilot Site field surveys are presented. Water samples were collected according to the field program described in Section 3.0. The results of the laboratory analysis were recorded in the Ministry's Sample Information System database along with the location and time of the sampling. The type of analysis performed is encoded in the parameter, and remark codes, and a numerical result, if applicable, is recorded.

One aspect of the laboratory technique that is an important consideration is the method detection level (MDL). The MDL is the lowest concentration of a contaminant that can be detected with a given method of analysis. The lab denotes samples where the concentration is below the MDL with the remark codes '<W' or '<'. Samples where the parameter was detected but in concentrations less than a certain value greater than the MDL are denoted '<T' indicating a tentative value. When the concentration of a parameter is large enough to give a reliable estimate of the sample concentration the remark code is '000'.

TABLE 4.1: PILOT MONITORING STUDY - SUMMARY OF WATERLOO STP DATA

Parameter	Influent*	Effluent*	Estimated Removal (%)
BOD_5 (5-DAY Biochemical Oxygen Demand) (mg/l)	138.79	12.75	90.8
COD (Chemical Oxygen Demand) (mg/l)	274.91	29.10	89.4
DOC (Dissolved Organic Carbon) (mg/l)	22.17	4.94	80.1
Total Ammonium (mg/l)	14.68	3.08	79.0
TKN (Total Kjeldahl Nitrogen) (mg/l)	22.11	4.34	80.4
Total Phosphorus (mg/l)	4.07	0.37	90.9
Residue, Particulate (mg/l)	114.88	7.29	93.7
Aluminum (μg/l)	640.0	100.0	84.4
Cadmium (μg/l)	10.0	0.0	100.0
Chromium (μg/l)	30.0	10.0	66.7
Copper (μg/l)	130.0	10.0	92.3
Mercury (μg/l)	0.24	0.02	91.7
Nickel (μg/l)	30.0	10.0	66.7
Zinc (μg/l)	100.0	30.0	70.0
Phenolics (mg/l)	0.60	ND	100.0
M - Cresol (μg/l)	54.41	ND	100.0
Phenol (μg/l)	18.95	ND	100.0
Butylbenzylphthalate (μg/l)	7.80	ND	100.0
2,4-Dichlorophenoxyacetic Acid (μg/l)	0.04	0.02	50.0
Silvex (μg/l)	0.06	ND	100.0
γ - BHC (μg/l)	0.01	0.01	0.0
pp - DDD (μg/l)	0.01	ND	100.0
Ethylbenzene (μg/l)	16.80	ND	100.0
M & P xylenes (μg/l)	16.94	ND	100.0
O-xylene (μg/l)	17.19	ND	100.0
1,2-Dichlorobenzene (μg/l)	21.54	ND	100.0
Chloroform (μg/l)	ND	1.55	N/A
1,1,1-Trichloroethane (μg/l)	ND	1.12	N/A
Tetrachloroethylene (μg/l)	ND	1.15	N/A

Source: Thirty Seven Municipal Water Pollution Control Plant - Pilot Monitoring Study, OME 1988.

* All values are geometric means / ND - Not detected / NA - Not applicable.

TABLE 4.2: FLUCTUATIONS OF TRACE CONTAMINANTS STUDY - SUMMARY OF WATERLOO STP DATA (GEOMETRIC MEANS)

Parameter	Influent*	Effluent*	Estimate Removal (%)
BOD_5 (5-day Biochemical Oxygen Demand) (mg/l)	110.0	4.7	95.7
FOC (Filtered Organic Carbon) (mg/l)	40.9	13.0	68.2
Residue, Particulate (mg/l)	105.0	5.5	94.8
Total Phosphorus (mg/l)	5.35	1.07	80.0
Filtered Phosphorus (mg/l)	2.45	0.52	78.8
TKN (Total Kjeldahl Nitrogen) (mg/l)	27.6	2.50	90.9
Total Ammonium (mg/l)	16.6	2.20	86.7
Cadmium (μg/l)	4.4	4.1	6.8
Chromium (μg/l)	46.7	27.3	41.5
Copper (μg/l)	110.0	13.5	87.7
Nickel (μg/l)	26.0	23.8	8.5
Lead (μg/l)	13.6	5.7	58.1
Zinc (μg/l)	135.0	74.9	44.
Phenolics tot. (μg/l)	16.2	2.7	83.
Benzene (μg/l)	1.4	0.3	78.6
Toluene (μg/l)	3.4	0.3	91.2
P&M-Xylene (μg/l)	8.3	0.3	96.4
Chloroform (μg/l)	2.8	0.8	71.4
1,1,1-Trichloroethane (μg/l)	1.1	0.6	45.5
1,4-Dichlorobenzene (μg/l)	1.7	0.8	52.9
Trichloroethylene (μg/l)	1.3	0.5	61.5
Tetrachloroethylene (μg/l)	1.1	0.5	54.5
0-Xylene (μg/l)	3.2	0.3	90.6
Ethylbenzene (μg/l)	1.4	0.3	78.6

Source: Fluctuations of Trace Contaminants in Municipal STPs (OME 1989)
* All values are geometric mean.

TABLE 4.3: FLUCTUATIONS OF TRACE CONTAMINANTS STUDY - SUMMARY OF WATERLOO STP DATA (VARIABILITY)

Parameter	Relative Standard Deviation (%)	
	Influent	Effluent
BOD_5 (5-day Biochemical Oxygen Demand)	52	32
FOC (Filtered Organic Carbon)	57	16
Residue, Particulate	115	34
Total Phosphorus	29	40
Filtered Phosphorus	43	64
TKN (Total Kjeldahl Nitrogen)	29	21
Total Ammonium	14	56
Cadmium	24	44
Chromium	77	50
Copper	47	29
Nickel	37	36
Lead	99	110
Zinc	51	38
Phenolics, total	60	61
Benzene	92	3
Toluene	150	50
P & M Xylene	680	70
Chloroform	220	60
1,1,1-Trichloroethane	71	60
1,4-Dichlorobenzene	100	30
Trichloroethylene	88	40
Tetrachloroethylene	77	20
O-Xylene	600	75
Ethylbenzene	670	9

Source: Fluctuations of Trace Contaminants in Municipal STP's (OME, 1989).

When a proportion of samples are in concentration less than that required for a remark code of '000' the sample set is said to be left-censored. The estimates of mean and variance may be biased unless special statistical estimating methods are used. For sample sets with a small proportion of non-detected samples a non-parametric description is useful in describing the population. Conversely, sample sets that have a high proportion of non-detects, estimates of the population parameters are difficult to make with confidence and the data is useful only as an indicator of presence or absence.

In general, the trace metal and conventional parameters have a large proportion of detections and the median water quality can be quantified and the variation of the water quality can be estimated. The organic parameters, however, were generally not detected except for a small number of parameters and then only in small proportion. The trace metal and conventional parameters are therefore considered as one category and the organics as a second category.

4.3.1 Trace Metals and Conventionals

In order to assess the impact of the Waterloo STP effluent discharge on the Grand River the sample data was combined into three groups. One group is a combination of the upstream sample locations excluding the Laurel Creek station. The second group is the combination of all the downstream groups excluding the storm weir and Breslube Creek. The third group is the combination of sample results from Laurel Creek and the storm weir. The first two groups are useful in determining the impact of the STP effluent and the third group is useful for characterizing the water quality of the major urban runoff tributaries. All the sampling data for the trace metal and conventional parameters are summarized in Box & Whisker plots in Appendix B. The Box and Whisker technique is a graphical one which plots the 25th and 75th percentiles of the data as the limits of the box and adds the median, 50th percentile, within the box. The tails of the plot are drawn to the next adjacent value that is within 1½ times the inter-quartile range, the difference between the 75th and 25th percentiles, of the limits of the box. Values beyond these limits are considered "outside values" and are plotted as points.

Table 4.4 is a summary of the median concentration values and the rate of compliance for the three sampling groups identified above. There are 40 parameters in this category of which 21 are trace metals and 19 are conventional parameters. Ten of the trace metals were rarely detected and were not included in Table 4.4. The

conventional parameters are physical and chemical constituents that have been traditionally used in the assessment of water quality.

TABLE 4.4: Instream Sampling Summary (in mg/l unless otherwise specified)

Parameter	PWQO[1]	Upstream Med. Conc.[2]	Upstream % Comp.	Downstream Med. Conc.[2]	Downstream % Comp.	Tributary Med. Conc.[2]	Tributary % Comp.
Copper	0.005	0.002	84.0	0.002	88.5	0.006	23.9
Lead	0.025	ND	96.2	ND	20.7	0.023	2.4
Zinc	0.03	0.004	93.6	0.007	89.6	0.040	46.5
Nickel	0.025	ND	100.0	ND	92.2	ND	96.4
Mercury	0.0002	ND	-	ND	-	0.010	-
Iron	0.30	0.210	64.4	0.290	56.8	0.880	24.7
Manganese	-	0.031	-	0.033	-	0.095	-
Aluminum	0.10[3]	0.190	-	0.230	-	0.595	-
Chromium	0.10	ND	100.0	ND	100.0	0.004	100.0
Strontium	-	0.250	-	0.280	-	0.380	-
Vanadium	-	0.001	-	ND	-	ND	-
Residue, filtered	-	280.0	-	308.0	-	643.0	-
Residue, part	-	12.0	-	11.95	-	20.8	-
DOC	-	5.4	-	5.5	-	4.45	-
Conductivity (umhos/cm)	-	443.0	-	471.0	-	525.0	-
pH (pH units)	6.5 - 8.5	8.37	84.4	8.39	-	8.15	8.15
Alkalinity (as $CaCo_3$)	-	169.25	-	169.0	-	220.1	-
Hardness (as $CaCo_3$)	-	202.75	-	211.0	-	307.0	-
Calcium	-	52.95	-	51.2	-	56.7	-
Magnesium	-	17.75	-	17.8	-	20.95	-
Chloride	-	21.20	-	30.0	-	199.0	-
Sodium	-	12.90	-	15.2	-	38.95	-
Fluoride	-	0.10	-	0.11	-	0.12	-
Ammonium	-	0.052	-	0.054	-	0.051	-
Nitrates	-	1.70	-	1.07	-	1.24	-
Nitrite	-	0.035	-	0.042	-	0.055	-
Kjeldahl N.	-	0.675	-	0.70	-	0.80	-
Phosphorus	0.034	0.06	4.7	0.051	-	0.052	0.52
Phosphate	-	0.012	-	0.018	-	0.017	-
Potassium	-	2.3	-	2.8	-	2.8	-

1 - Ontario Provincial Water Quality Objective except where noted.
2 - All units mg/l unless otherwise specified.
3 - CCREM, 1987
4 - Ontario Provincial Water Quality Guideline

Conventionals

The turbidity of water is connected with the presence of suspended and colloidal substances forming mixtures of solid organic and mineral complexes. The suspended solids also consist of metal hydroxides, phytoplankton, and zooplankton. Some of this organic particulate is oxygen-demanding in natural water. Filtered residue shows higher levels downstream than upstream with median values of 308.0 and 280.0 mg/l respectively, while the particulate residue shows little difference at 12.0 mg/l. The sampling at the confluence of the two tributaries with the Grand River, Laurel Creek and the storm weir, showed elevated filtered residue of 643.0 mg/l and particulate residue of 20.0 mg/l for the median values of the samples. Dissolved organic carbon appears to be constant at 5.4 mg/l upstream and downstream.

A rough index of total dissolved substances is the measure of electrical conductivity. Conductivity is determined by the presence of substances which dissociate into cations and anions and is often carried out to establish contributions from runoff waters and impact areas such as mixing zones. Conductivity shows an increase from 443 umhos/cm upstream to 471 umhos/cm downstream. The runoff tributary stations exhibit higher levels of conductivity of 525 umhos/cm.

Other important parameters of physical water quality are pH, alkalinity and hardness. These parameters are inter-related as well as being correlated with the solubility of many other parameters particularly the metals. These parameters are of special importance as modifiers of bioavailability of contaminants, especially trace metals, which is reflected in the dependence of several criteria on them. In pure natural water, the values of pH are dependent on the concentration of free carbon dioxide, bicarbonate and carbonate ions. The pH ranged from 7.4 to 8.8 in the survey samples. The upstream and downstream values show little variation and the median value was approximately 8.4. The tributaries, Laurel Creek and the storm weir showed a slightly depressed pH at 8.2 with much greater variation.

Alkalinity is measured by the vloume of a strong acid solution required to neutralize the cations of weak bases such as bicarbonates, carbonates and organic acids. This titration value is expressed as mg/l of $CaCO_3$ (Calcium Carbonate). The median instream alkalinity is 169.0 mg/l (upstream and downstream) and that of the combined tributaries is higher at 220.0 mg/l of $CaCO_3$ and again the variability of alkalinity at these stations is much greater than the other instream stations.

The total hardness of water is made up of cations of alkali earth metals, mainly calcium and magnesium. High levels of calcium and therefore total hardness is typical of southern Ontario rivers due to the presence of carbonate rock. Like alkalinity, hardness is expressed as mg/l of $CaCO_3$ and the median hardness is 202.0 mg/l upstream and 211.0 mg/l downstream. The tributary median is very hard at 307.0 mg/l of $CaCO_3$.

Calcium values are 53.0 mg/l and 51.2 mg/l, for the upstream and downstream stations respectively. Tributary calcium had a measured median value of 56.8 mg/l, slightly elevated. Similarly, the concentrations of magnesium upstream and downstream are virtually the same at 17.8 mg/l with the tributary median concentration at 21.0 mg/l.

Chlorides are formed in practically all natural waters. Anthropogenic sources of chlorides often involve large contributions from municipal sewage discharges, urban storm water runoff, road de-icing and industrial wastes. Table 4.4 shows the relatively large increase in the median concentrations of chlorides from 21.2 mg/l upstream to 30.0 mg/l downstream of the Waterloo STP. The urban runoff tributaries have a median chloride concentration of 199.0 mg/l. Sodium salts are often associated with the same sources and show the same patterns instream in this stretch of the Grand River with concentrations upstream of 12.9 mg/l, downstream 15.2 mg/l and tributaries 39.0 mg/l. These two ions tend to remain in water without significant interaction with suspended solids or biota and hence are a simple indicator of the presence of sources of the type discussed. Clearly major sources

of these two species are Laurel Creek and the storm weir. Concentrations of the dissolved fluorides shows the third greatest difference, after chloride and sodium, in water quality upstream and downstream of the STP.

The common salts of potassium are highly water soluble and resist partitioning in water. Its occurance in natural waters results from contact with potassium-bearing soils and industrial wastes. The median upstream level was 2.3 mg/l and the downstream level was 2.8 mg/l.

Filtered ammonia nitrogen in unpolluted waters is connected with biochemical decomposition of protein substances and form reduction of nitrites and nitrates in the water. The relationship between ammonium ion concentration and free ammonia is strongly determined by the pH and to a lesser degree, temperature. Filtered nitrite is an intermediate oxidation product of ammonia and filtered nitrate is the end product of biochemical processes. Nitrates are also present in fertilized agricultural areas. In unpolluted rivers nitrate nitrogen concentration is generally less than 0.5 mg/l and in the Grand River the median concentrations are 2 to 3 times this level (1.0 mg/l to 1.7 mg/l). Total Kjeldahl nitrogen (TKN) is a measure of total nitrogenous matter excluding nitrate and nitrite nitrogen. TKN minus the ammonia nitrogen concentration gives a measure of organic nitrogen. TKN median concentrations are above the levels of 0.1 to 0.5 mg/l normally found in unpolluted water.

Phosphorus is a primary nutrient for plant growth and is involved in the cycles of photosynthesis and decomposition. Although there is no firm criterion for total phosphorus, a level of less than 0.03 mg/l should be sufficient to prevent excessive plant growth. With respect to this guideline the Grand River has high levels of this nutrient. Median values of phosphorus are in the range 0.05 to 0.06 mg/l with over 90 percent of the observations exceeding 0.03 mg/l. Filtered reactive phosphate is considered to be the bioavailable fraction of total phosphorus.

Metals

Twenty-one trace metals were sampled in the Grand River Pilot Site Study of which 10 were rarely detected. These trace metals are silver, arsenic, free cyanide, available cyanide, barium, boron, beryllium, cobalt, selenium, and cadmium. Of the remaining eleven trace metals, eight have associated PWQOs although the criterion for aluminum is from the Canadian Water Quality Guidelines (CCREM, 1987).

Copper salts occur in natural surface waters at levels typically less than 0.005 mg/l. The PWQO for copper is 0.005 mg/l and the study area is in compliance more than 84 percent of the time with upstream and downstream median levels of 0.002 mg/l. The tributary samples, however, have a median value of 0.006 mg/l and is in compliance only 23.9 percent of the time. Hardness of receiving water ameliorates the toxicity of copper somewhat through its increased tendency to sorb to fine particulate matter.

Lead in unpolluted natural water is a trace contaminant. Anthropogenic sources of lead are industrial effluents, lead plumbing and to a large extent, automobile exhaust. Lead is a bioaccumulative parameter whose toxic effect is decreased by increased hardness, alkalinity and dissolved oxygen. The PWQO for lead is stated in terms of alkalinity as follows.

Pb criterion mg/l	Alkalinity mg/l as $CaCO_3$
0.005	< 20
0.010	20 - 40
0.020	40 - 80
0.025	> 80

For the Grand River Pilot Site Study with median alkalinity of approximately 170.0 mg/l the objective is therefore 0.025 mg/l of lead. Median lead levels upstream are non-detected but show a non-compliance rate of 96.2 percent. Downstream median lead levels are also less than the MDL for lead and show increased non-compliance

rate of 20.7 percent. The tributary lead median value is just under the PWQO at 0.023 mg/l.

Zinc occurs generally in only trace amounts in natural waters. It's fate is usually as a complex with particulate matter which settles out of suspension. Zinc is toxic to micro-organisms and it's toxicity decreases with increasing hardness. Zinc is in compliance with the PWQO of 0.03 mg/l approximately about 90 percent of the time except at the confluences of Laurel Cr. and the storm weir where it is out of compliance more than 50 percent of the time.

Nickel acts similarly to most trace metals in it's propensity to form complexes with particulate matter. In the Grand River Pilot Site Study the nickel levels are in compliance more than 90 percent of the time.

Total mercury concentration in unpolluted freshwaters are generally less than 0.1 $\mu g/l$. Total mercury in filtered samples should not exceed 0.2 $\mu g/l$. This objective is not directly applicable to the samples collected as part of this study which are unfiltered totals. Most of the mercury is present in fine particulates and therefore would be removed by filtration. Over 50 percent of the samples at the upstream and downstream sites were below the MDL. In the tributary samples mercury was detected more than 50 percent of the time.

Iron is present in most surface waters and it's concentration is determined by geological structure, hydrological conditions, physiochemical and biochemical factors. These factors also affect the correlation of concentrations for various forms of iron. The most important factors are pH, redox potential, content of oxygen, carbonic acid, hydrogen sulphide, organic substances which form complexes with iron and the microflora. In fresh waters, iron concentrations are generally less than 0.5 mg/l. Ontario has set a PWQO of 0.3 mg/l to protect aquatic biota. Iron levels in the Grand River Pilot Site area are high relative to the PWQO with

compliance rates of 64.4 percent upstream, 56.8 percent downstream and 24.7 percent in the tributary samples.

Manganese is similar to iron in that it is found in many industrial wastes and occurs in soils as manganic and manganous compounds. There is no PWQO for manganese. Upstream and downstream samples have median concentrations of approximately 0.03 mg/l with the tributary median of 0.1 mg/l.

In surface waters, aluminum ions may result from industrial wastes or wash water from drinking water treatment plants. From Table 4.4 we can see that the aluminum levels in the tributary site were much higher than the other instream sampling stations.

Chromium is a trace element in surface waters and is strongly sorbed to particulate matter. Metal plating and chemical processing are the most common anthropogenic sources of chromium. The Grand River showed relatively low levels of chromium in comparison with the PWQO of 0.1 mg/l.

Strontium was detected in virtually all samples as can be expected for this type of surface water. The median concentration values for upstream and downstream locations are 0.25 and 0.28 mg/l respectively. The median value for the combined Laurel Creek and storm weir samples was 0.38 mg/l.

4.3.2 Organics

The second category of parameters, the organics, was considered separate from the trace metals and conventionals due to the differences in the chemistry of these two categories. A major proportion of the organic compounds are solely anthropogenic. Many are nonpolar and hydrophobic and are found dissolved in water in only micromolar concentrations, if at all. A large number of parameters that were tested were not detected at any station (71 percent).

This can be accounted for, for two reasons. Firstly, the method detection level (MDL) is high compared to instream concentration levels. Secondly, the organic parameters follow a complicated fate and pathway mechanism where the water column compartment levels may be very small in comparison with other compartments such as volatization to air, binding with sediments and uptake by biota.

The high relative proportion of non-detects in the sampling survey analysis makes a quantitative approach impossible and consequently presence/absence approach was adopted. A parameter therefore may fall into one of four categories. These categories are listed in Table 4.5 with the number of parameters in each category representing sampling at all sites.

TABLE 4.5: ORGANIC PARAMETER DETECTION SUMMARY

Parameter Category	Number of Parameters
Detected - in measurable concentration	21
Detected - tentative value only (<T)	16
Tested for but not detected (<W)	89
Not tested *	37
Total Parameters	163

* Not tested due to one of the following:
- no sample
- sample destroyed
- sample wrongly submitted etc.

In instances where a measurable concentration was obtained in some samples, the proportion of these values to tentative or non-detected samples was low and for that reason estimates of median, mean or variance were not made.

Table 4.6 shows the subset of 36 parameters that were detected at least once at any station ranked according to the percentage of sites where the parameter was found to the number of sites where the parameter was tested.

The sites with the highest proportion of different parameters detected were site #2, Laurel Creek and Site #8, the Storm Weir. This finding is consistent with the levels of trace metals and conventionals from the previous section.

The most prevalent parameter detected in the water column was BHC-gamma (Lindane). Lindane is a veterinary pesticide that is known to be persistent in the environment. It's source is probably a diffuse one from the predominantly agricultural upstream watershed. Lindane was detected at 12 of 15 stations. The second most commonly detected parameter was BHC-alpha.

TABLE 4.5: Organic Parameter Detection Frequency

Parameter Name	Site Number 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	% of Stations with detections
BHC-gamma (Lindane)	3	D		D	1	D	D	D	D	D	D	T	T		D	T	1	80.0
BHC-alpha	D	D		D	T		D						D		T	T	D	66.7
pentachlorophenol	T	2			2			D							T	T	1	57.1
1,2,3-trichlorobenzene	T	1		T	1	T							D		T	T	T	33.3
diethylphthalate	T	T			T								T			D	T	33.3
Aldrin	D	D	D	T	T	T							T		T	T	T	30.0
tetrachloroethylene	T	3	T					7							T	T	T	28.5
2,4-DP	T	T		T	1		T						T			T	1	25.0
di-N-butylphthalate	T	T	T		T			T							T	D	T	25.0
O-xylene	T	T	1		T			2					T		T	T	T	22.2
1,2,3,4-tetrachlorobenzene	T	1	T	T	T								T		T	T	1	22.2
2,6-dinitrotoluene	T				T								T			D	T	20.0
PP-DDT	D	D		T	T	T	T	T	T	T	T	T	T		T	T	T	20.0
Dicamba	T	D	T	T	1	T							T	T		T	T	20.0
hexachloroethane	T	T			3								T				T	20.0
2,4-dichlorophenoxyacetic	T	T		T	1	T	T	D	T	T	T	T	T		D	T	T	20.0
1,4-dichlorobenzene	T	T			1			T							T	T	T	14.2
1,3-dichlorobenzene	T	T			1			T							T	T	T	14.2
1,2-dichlorobenzene	T	T			1			T							T	T	T	14.2
2,3,5,6-tetrachlorophenol	T	T			T	T	T	T	D	T	T	T	T	T	D	T	T	13.3
toluene	T	4	T		1								T		T	T	T	12.5
2,4,5-trichlorophenoxyacetic	T	T		T	T		T						T			T	1	12.5
Chlordane-gamma	T	D	T	T	T								T			T	T	12.5
OP-DDT	T	D		T	T		T						T			T	T	12.5
PP-DDD	T	D		T	T		T						T			T	T	12.5
PP-DDE	T	T		T	T		T						D			T	T	12.5
phenol	T	T	1		T								T		T	T	T	12.5
1,1-dichloroethylene	T	T	T		3			T					T		T	T	T	12.5
trihalomethanes total	T	T			2			T					T		T	T	T	12.5
1,1,1-trichloroethane	T	4	T		T			T					T		T	T	T	11.1
M-xylene	T	T	T		T			2					T		T	T	T	11.1
pentachlorobenzene	T	D		T	T	T							T		T	T	T	11.1
Chlordane-alpha	T	D	T	T	T	T							T			T	T	11.1
Dieldrin	T	D	T	T	T	T							T		T	T	T	10.0
2,4,5-trichlorotoluene	T	T		T	1	T	T	T	T	T	T	T			T	T	T	7.1
octachlorostyrene	T	T	T	T	1	T	T	T	T	T	T	T	T		T	T	T	6.2

Legend:
T - Parameter tested for but not detected
D - Parameter detected, tentative value only

A number signifies the number of measurements above a tentative value.
Parameters are ranked in order of their percentage of number of stations detected to number of stations analysed.

5.0 ANALYSIS AND MODELLING

5.1 Statistical Assessment of Water Quality Data

One of the purposes of this section is to examine the "noise" of the sampling data. Noise refers to the scatter or overall variation within the data. Statistical tests indicate that the noise of the water quality data masks major effects from the Waterloo STP loading and precipitation. Noise contributions arise from laboratory imprecision, bias in sampling, and the natural variation of instream water quality. Sampling surveys must be designed to reduce bias in the sampling data to a minimum. Bias is the error in estimates of statistical parameters, such as the mean and the variance caused by improper sampling procedure. The contribution to error from laboratory imprecision should be quantified with the use of quality assurance and quality control (QA/QC). QA/QC relys on a standardized program consisting of the submission of replicate samples, blanks and spiked samples. The noise due to lab analysis can then be quantified. When bias is minimized and lab error is quantified, instream water quality variation can be estimated with greater accuracy. QA/QC procedures were not performed for the Grand River Pilot Site sampling survey and so the variance of water quality is overestimated.

Due to the limited sensitivity of laboratory tests a method detection level (MDL) can be defined which is generally the lowest concentration that can be measured. Concentrations of pollutants in samples which are below the MDL are reported as non-detects. The presence of non-detects in sampling data produces left censored data. Left censoring can significantly bias estimates of the mean and variance of the population if not accounted for. Nonparametric methods were used to minimize these biases.

In this section, hypotheses about instream concentrations data are tested, sources of bias and error are investigated and inferences about the sample populations are used as input to water quality models. Visually, the Box and Whisker representation (Appendix B) of the sampling data showed little, if any, downstream trends in water quality. Sites 2 (Laurel Creek), 5 (STP outfall), and 8

(Storm Weir) showed elevated levels of almost all parameters which may represent urban runoff not yet fully mixed with the river. For this reason the data from these sites was not used in the ambient water quality analysis or the modelling exercise. We need to determine if the variation of concentration between stations is significantly greater than the variation between samples of each station indicating an impact from the Waterloo STP.

The Kruskal-Wallis test, or H-test, is a non-parametric alternative to a one-way analysis of variance and was used to test the null hypothesis that independent samples came from identical populations against the alternative that the means are not all equal. In this context, 'sample' refers to a set of observations. In the Kruskal-Wallis test the k samples are ranked from low to high as though they constituted a single sample.

The hypothesis that the ambient water quality concentrations are the same upstream and downstream of the Waterloo STP was tested. The alternative hypothesis is that the STP effluent has a significant impact on water quality. The sampling sites are divided into upstream and downstream groups. The Kruskal-Wallis statistic was calculated for each of the 30 parameters for which sufficient sample data was available. These are the same parameters as in the Box and Whisker plots. The calculated statistic was used to rank the parameters in the order of the relative difference of their upstream and downstream mean concentration (Figure 5.1). The first eleven parameters above the middle horizontal line of Figure 5.1 have mean values significantly higher at the downstream site than the upstream site.

Wet weather precipitation events are known to affect river water quality and that hypothesis was tested. For the same 30 parameters the hypothesis that wet and dry weather samples were from the same population was accepted under the Kruskal-Wallis test. The sample data does not indicate differences in water quality due to precipitation. This may be due to sampling bias from failure to adequately define wet and dry weather and insufficient data from wet weather sampling. In order to define a cause and effect

relationship for precipitation and water quality the entire watershed and its precipitation record must be examined carefully. Water quality samples taken during a local dry weather day may represent wet weather water quality due to prior precipitation events upstream in the watershed.

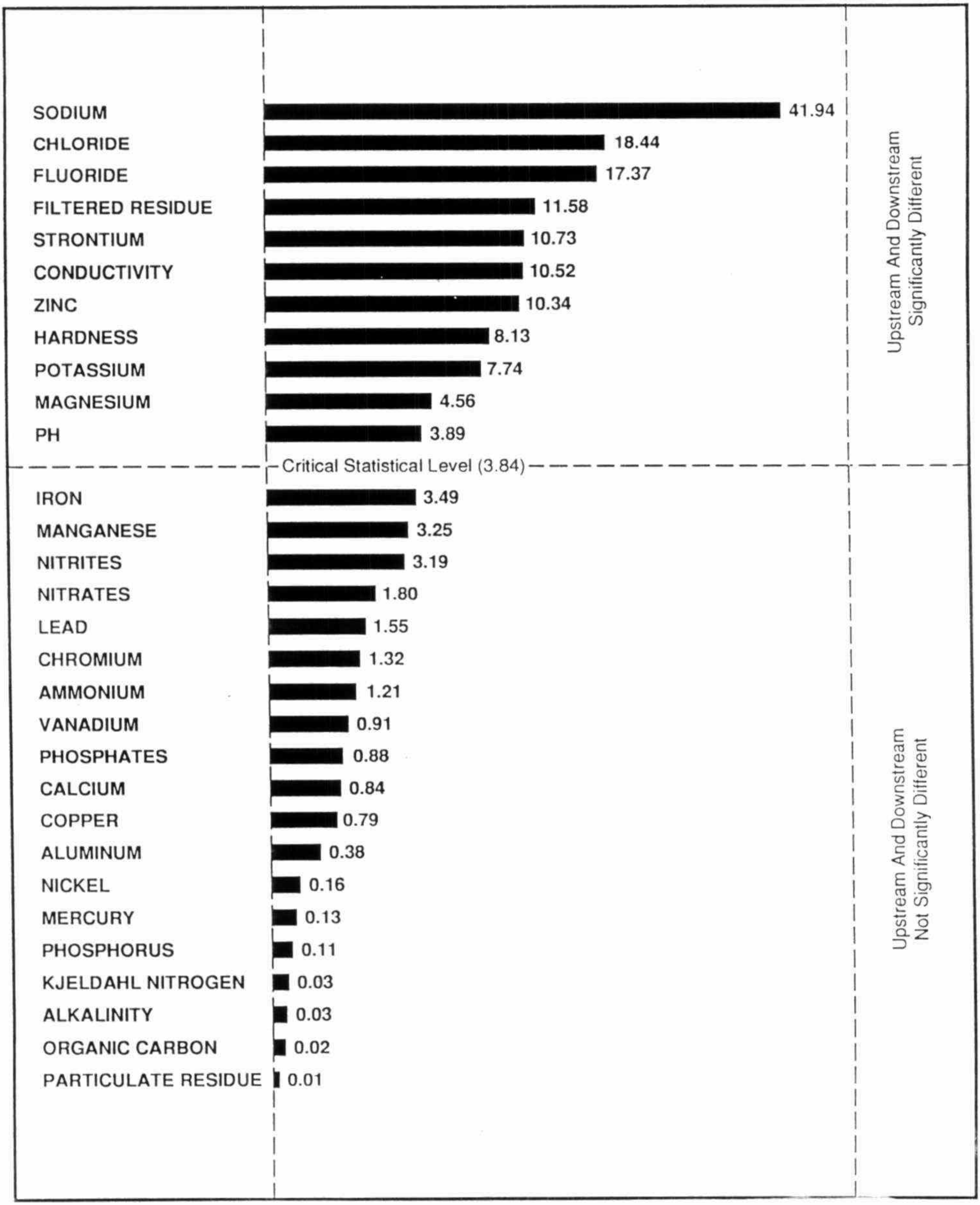


Figure 5.1: Parameters Ranked by Significance of Difference Between Upstream and Downstream

5.2 Water Quality Modelling

To make inferences and predictions based on sample data, mathematical models were used. More complex models require a larger amount of data and yield more detailed results. The balance between field survey costs and data requirements necessitates careful planning to make economic use of resources. The models used in the Grand River Pilot Site water quality component are presented in a logical progression from a simple dilution model to a much more complex water quality predictive model. The available quality and quantity of sample data was the limiting factor in the sophistication of the models and their predictions. Non-parametric descriptions are used for ease of interpretation, however, some of the populations are assumed to be log normally distributed for modelling purposes. The following models were used and the results are presented.

5.2.1 Mass Balance Model

The mass balance model is the simplest model commonly used in impact assessment. It is a simple dilution model described by the following equation.

$$C_M = \frac{C_B * Q_B + C_E * Q_E}{Q_B + Q_E}$$

where:

C_B = Background concentration

Q_B = Upstream river discharge rate

C_E = Effluent concentration

Q_E = Effluent discharge rate

C_M = Fully mixed downstream concentration

This approach cannot estimate the frequency distribution of downstream water quality nor the discharge quality required to achieve set mean or percentiles of downstream water quality. It is, however, the simplist method for estimating a mean or median water quality value for specific design conditions.

Assessment of different scenarios is accomplished by a choice of design conditions such as the extreme low river flow and peak effluent flow rate. The results for two different effluent flows are shown in Table 5.1. In both cases median values of sample concentrations are used. Effluent limits are generally calculated to protect water quality at critical low flows such as the 7Q20. The Grand River is a regulated river and the critical low flow is taken as the low flow regulation target of 8.4 m^3/s. The lower effluent flow rate of .46 m^3/s is the median flow rate of the condition existing at the time of the survey and the effluent flow rate of 1.315 m^3/s represents the peak projected flow rate for an average design capacity of 72,700 m^3/day (0.841 m^3/s). Only parameters that were measured in the effluent in the dynamic fluctuation study were used. Of these parameters, for which background concentrations are not known, the background concentration was taken as zero for a straight dilution calculation.

The only two parameters projected to exceed criterion levels were cadmium under the ultimate STP design capacity and total phosphorus under both STP flow scenarios. It should be noted that total phosphorus also exceeds the criterion in the background water quality.

TABLE 5.1: **Mass Balance Calculations.**

River Flow Rate = 8.4 m^3/s

Parameter	Median Effluent Concent. (mg/l)	Median Background Concent. (mg/l)	Effluent Flow Rate = .46 m^3/s Daily Load (kg)	Effluent Flow Rate = .46 m^3/s River Concent. (mg/l)	Effluent Flow Rate = 1.315 m^3/s Daily Load (kg)	Effluent Flow Rate = 1.315 m^3/s River Concent. (mg/l)	Criteria (mg/l)
Cadmium	0.004	-	0.16	0.00020	0.457	0.00054	0.0002
Chromium	0.028	0.0025	1.11	0.0038	3.182	0.0060	0.10
Copper	0.014	0.0015	0.56	0.0021	1.589	0.0032	0.005
Nickel	0.023	0.0020	0.91	0.0031	2.613	0.0048	0.025
Lead	0.006	0.0050	0.24	0.0051	0.680	0.0051	0.025
Zinc	0.076	0.0050	3.02	0.0087	8.636	0.0146	0.030
Kjeldahl N	2.500	0.690	99.40	0.780	284.0	0.935	
Phosphorus	1.070	0.058	42.53	0.111	121.6	0.195	0.030
Ammonia Tot.	2.190	0.051	87.04	0.162	249.0	0.309	
Phenols	0.0028	-	0.111	0.00015	0.317	0.0038	0.001
Benzene	0.00028	-	0.011	0.000015	0.032	0.000038	0.300
1,1,1-trichloroethane	0.00064	-	0.025	0.000033	0.071	0.000087	
Chloroform	0.00084	-	0.033	0.000044	0.095	0.00011	1.2
O-xylene	0.00048	-	0.019	0.000025	0.055	0.000065	
1,2-dichlorobenzene	0.00095	-	0.038	0.000050	0.110	0.00013	0.002
ethyl benzene	0.00050	-	0.020	0.000026	0.057	0.000068	0.70
1,4-dichlorobenzene	0.00083	-	0.033	0.000043	0.094	0.00011	0.004
trichloroethylene	0.00052	-	0.021	0.000027	0.059	0.000070	0.094
toluene	0.00030	-	0.012	0.000016	0.034	0.000041	0.030
m&p-xylenes	0.00035	-	0.014	0.000018	0.040	0.000047	0.040
tetrachloroethylene	0.00097	-	0.039	0.000050	0.110	0.00013	0.260

A major weakness of this model is that it does not effectively consider variability in upstream flow and water quality. The frequency of simultaneous occurrences of critical conditions is unknown in this formulation. To examine this aspect of water quality variability a Monte Carlo formulation was used.

5.2.2 Monte Carlo Simulation

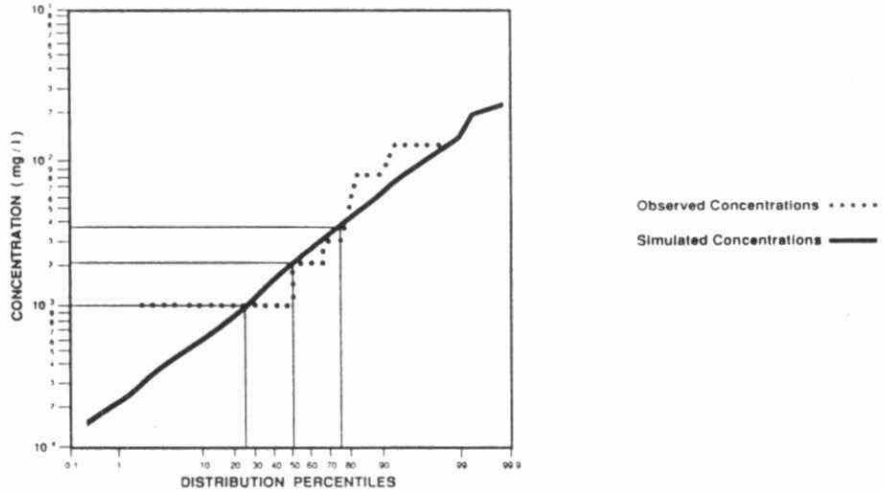
The Monte Carlo method utilized a deterministic water quality model to repetitively calculate downstream concentrations based on new randomly chosen inputs from each calculation. The deterministic water quality model utilized was the mass balance model described in the previous section. Each input was produced by a random number generator in the case of effluent flow rate, effluent concentration and upstream concentrations. Real observed data was used for upstream flow rates. Computed concentrations were evaluated collectively to represent downstream response. A disadvantage of the Monte Carlo method is its inability to account for significant cross correlations between different types of probability distributions. Cross correlations between flows and concentrations are sometimes observed in streams, however the Monte Carlo mass balance has been shown to be quite insensitive to the level of cross correlation that is typical in the Grand River (Marr & Canale 1988).

Figure 5.2 illustrates the input data for copper as plotted on log normal probability paper with the vertical axis as logarithm of concentration or flow and the horizontal axis as the probability of the distribution.

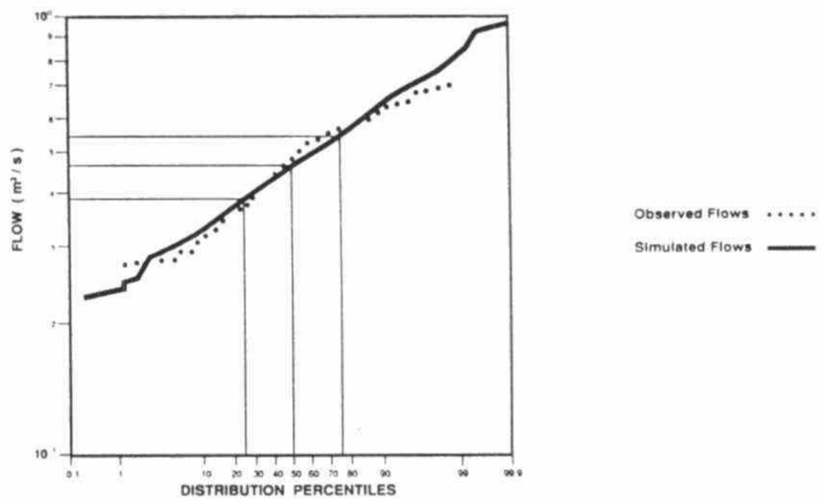
The variables of effluent concentration, effluent flow and background river concentrations were assumed to be log normally distributed; a common assumption which was borne out by the data set. By estimating the median and quantiles of the observed data, a set of 1000 random deviates were produced using a random number generator, for each of the input variables. River flow was found

to be not log-normally distributed primarily due to flow regulation of the river. This deviation from log-normality is apparent in the log-normal probability plot of river discharge. On log-normal probability paper, log normally distributed data fits a straight line. We have, however, 5 years of daily river flow data from the GRCA streamflow gauge at Bridgeport and 1000 randomly selected observations were used for inputs directly into the model.

BACKGROUND CONCENTRATIONS - Observed & Simulated



EFFLUENT DISCHARGE RATES - Measured & Simulated



BACKGROUND CONCENTRATIONS - Observed & Simulated

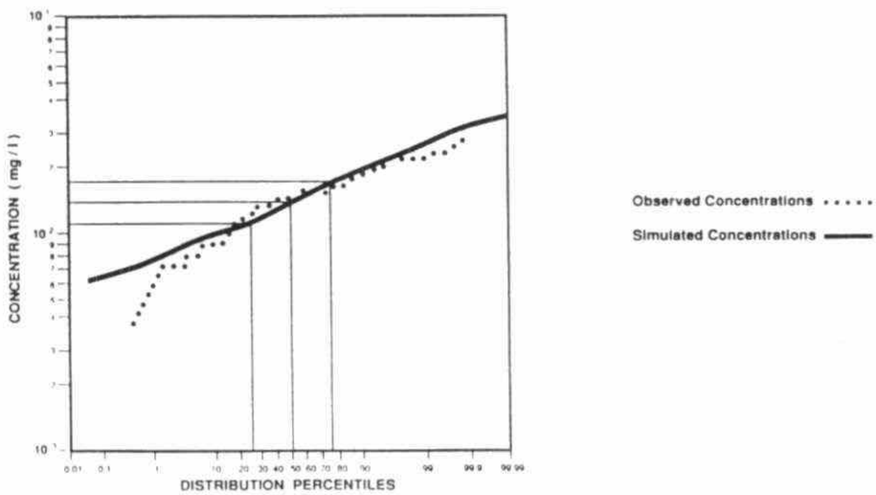


Figure 5.2: Input Data for Monte Carlo Simulation for Copper

Although we have upstream and downstream concentrations for 30 trace metal and conventional parameters, and 24 parameters were sampled in the effluent, only 10 parameters were in both groups and only these parameters were modelled to produce estimates of downstream concentrations. For the 11 organics sampled for in the dynamic fluctuation study report plus cadmium, phenols and filtered phosphorus, there were no estimates of upstream and downstream concentrations. Inferences about water quality impact from a point source discharge can only be made in conjunction with background concentrations and hence these calculations are presented for information about total loading from the STP.

The log normal probability plots of the simulation results (Appendix C) show two curves composed of unconnected symbols. As illustrated in the legend one curve is the 1000 upstream random concentration deviates and the other is the 1000 downstream predicted concentrations. When a water quality criterion was available for a parameter it is shown on the graph as a dashed horizontal line and the legend indicates the percentage frequency of non compliance for both the upstream and downstream distributions.

The downstream observations from the sampling survey were ranked, transformed and linearly regressed in the log normal probability space to plot the oblique dashed time on the plots as a visual comparison to predicted concentrations. For lead, zinc and nickel only, does the observed downstream concentration have a greater frequency of excursions than the predicted concentrations. This is likely due to other sources of these three parameters such as Laurel Creek, the Storm Weir and diffuse sources.

The plot of total ammonia shows an observed downstream concentration significantly lower than that predicted. The statistical analysis shows that total ammonia concentrations were not significantly different upstream from downstream and yet the Monte Carlo simulation predicts an impact from the relatively large

load of ammonia from the Waterloo STP. This can be explained by the fact that ammonia is not a conservative substance but decays in time due to sunlight, aeration and pH. Considering that the amount of decay is assumed to be dependent on time, and hence distance downstream from a source, this aspect was not modelled because a specific downstream location would have to be chosen and this was not done for the sake of uniformity.

5.3 Effluent Limits

One of the main objectives of the Grand River Pilot Site Study was the setting of effluent limits for the Waterloo STP for those parameters where the STPP can be shown to contribute to a significant increase in the rate of noncompliance in the receiver. The Ministry publication "Water Management" (OME, 1984) outlines the intent of the water management policies and specifies procedures to implement those policies.

Two of the policies that will be used in setting effluent limits are as follows:

Policy 1: In areas which have water quality better than the Provincial Water Quality Objectives, water quality shall be maintained at or above the Objectives.

Policy 2: Water quality which presently does not meet the Provincial Water Quality Objectives shall not be degraded further and all practical measures shall be taken to upgrade the water quality to the Objectives.

In the preceding sections parameters have been identified that show statistically significant increases in instream concentration due to the STP, based on the data collected in the field study and parameters that show increases in non-compliance in the modelling exercise. This component of the Grand River Pilot Site Study has considered fully mixed instream concentrations only and the effluent

limits presented in this section reflect that viewpoint. More stringent effluent requirements may be developed based on the size of the mixing zone with respect to the regulatory mixing zone requirements (OME, 1990).
Effluent requirements are applicable to only those parameters that have a PWQO/G or other criterion as well as numerical estimates of instream concentrations. This constraint precludes us from the setting of effluent limits for any of the organic compounds sampled in this study. Many of the conventional and trace metal parameters do not have a criterion available.

There are four parameters that have a criterion, instream concentration estimate and effluent concentration estimate. Modelled via the Monte Carlo Simulation approach, these four parameters were shown to cause increased non-compliance above a compliance rate of 95 percent and therefore require effluent limits to comply with Policy 2 (see Table 5.2). It was assumed that a compliance rate of 95 percent represented a Policy 1 situation.

TABLE 5.2: Non-compliance Levels for Simulation Results

Parameter	Percent Non-compliance Upstream	Downstream	Percent Increase
copper	13.1	15.4	2.3
zinc	7.4	8.0	0.6
phosphorus	82.3	92.7	10.4
lead	5.9	6.2	0.3

Figure 5.1 in Section 5.1 indicated that there were no significant differences between the sampled upstream and downstream concentrations for lead, copper and phosphorus. This table indicated, however , significant differences for zinc while the modelling exercise suggests that the STP's contribution to be a 0.6 percent increase in non-compliance. This could be explained by considering that there are two primary sources of urban runoff situated near the STP outfall.

Conversely, the modelling exercise suggests a greater than 10.0 percent increase in phosphorus levels due to the STP effluent while Figure 5.1 indicated no significant difference between upstream and downstream concentrations. The downstream concentration distribution is a composite distribution of the samples from several downstream stations and for this reason, the instream decay of phosphorus concentration due to uptake by aquatic flora was not modelled. Phosphorus levels instream are in the Policy 2 category and therefore the effluent limits are required to ensure no further degradation of the receiving water quality. This implies directly that an effluent quality better than or equal to the background quality is required. This means that the median effluent concentration of phosphorus should be reduced from 1.027 mg/l to .0792 mg/l or a reduction of 92.3 percent.

The modelling results of the trace metal parameters lead, zinc and copper show that the STP's contribution to the rate of non-compliance to be relatively small. It is likely not economical to require a greater level of effluent treatment to decrease the STP's disharge load of these parameters to the small extent that is required.

The probablistic framework of Monte Carlo modelling has the advantage over the simple mass balance in that we can take into account the variablity of pollutant concentrations and flow rates, both in the effluent and the receiver. This allows for an analysis of the frequency of non-compliance. Thus the task of setting effluent limits is one of determining the mean effluent concentration and the variance of the concentrations that is required to meet the PWQOs. A factor which should be considered, therefore, is how an improvement in a treatment process affects the mean and variance of the effluent quality distribution. Equivalently, how can the inputs to the model be defined to reflect an improved discharge quality. Modelling results have indicated that effluent concentration variability has little effect on mixed

instream water quality except for cases of relatively low dilution ratios; in the range of four to one or less.

The effluents effect on the rate of non-compliance in the receiver was demonstrated in the modelling section. For a set specific river water quality a discharge quality required to achieve this must be determined. This can be done by making an initial guess of the discharge quality and calculating the level of non-compliance from the Monte Carlo model. The discharge quality can then be progressively amended until the target river quality is achieved. This initial guess for the discharge quality is made by scaling down the median effluent concentration as well as scaling down the variance of the effluent concentration.

The Policy 2 situation for phosphorus was modelled and the results are shown in Table 5.3. The numbers in the interior of the table represent the increase in the percentage rate of non-compliance for an effluent quality defined by the change of median and the change of variance of the effluent concentrations indicated by the rows and columns respectively. The modelling results agree closely with the initial estimate of a reduction in the median concentration of 92 percent. Table 5.3 also shows that the situation is insensitive to changes in the variance.

TABLE 5.3: Percent Increase in Non-compliance for Phosphorus

Percent Decrease in median	Percent Decrease in Variance Effluent Concentration				
	0	20	40	60	80
0	10.80				
50	6.32	6.00	5.82	5.30	6.11
75	2.62	2.80	2.40	2.66	2.29
90	1.83	1.15	0.77	1.03	1.73
92	0.63	0.47	-0.26	0.32	0.90
95	-0.54	-0.44	-0.61	1.2	-0.5

The insensitvity of instream water quality to effluent quality variability is due to the relatively high dilution ratio. For the Waterloo STP the ratio of the median effluent flow rate to the median upstream river flow rate is approximately 70 to 1. The dilution ratio for the median effluent flow rate and the river low flow (7Q20) is more than 18 to 1.

To illustrate the iterative method of determining effluent limits using the Monte Carlo formulation, a hypothetical scenario will be presented. Table 5.4 outlines the existing condition.

TABLE 5.4: Hypothetical Scenario Initial Conditions

Effluent Concentration	Median =	0.0137 mg/l
	75th Percentile =	0.0178 mg/l
Background Concentration	Median =	0.00021 mg/l
	75th Percentile =	0.00036 mg/l
Effluent Flow Rate	Median =	8.4 cms
	75th Percentile =	10.5 cms
River Flow Rate	Median =	21.3 cms
	75th Percentile =	42.8 cms
	Low Flow (7Q20) =	8.1 cms
Criterion = 0.005 mg/l		

From this data it can be seen that the lowest dilution ratio is less than 1 to 1. The Monte Carlo model was run for 10,000 deviates of each distribution to predict downstream compliance. For the initial or existing condition the background was in compliance more than 99.99 percent of the time. The downstream rate of noncompliance predicted by the model was about 36.5 percent of the time indicating a significant increase in instream concentration of our hypothetical contaminant attributable to the discharge.

The effluent concentration distribution is scaled to produce guesses of the effluent limit and a random number generator produced 10,000 random deviates for use in the model. The Monte Carlo model was run to estimate the rate of non-compliance that

results from the new effluent quality deviates. This was performed repeatedly until a criterion was met. It was assumed that for this substance a compliance rate of 95 percent was necessary. Table 5.5 summarizes the results for several of the Monte Carlo runs. The numbers in the interior of the table indicate the rate of non-compliance for that particular run. From the table it can be seen that for no change in the variance a 55 percent decrease in the median effluent concentration is required to achieve a compliance rate of at least 95 percent. This is equivalent to a median concentration of 0.0062 mg/l and a 75th percentile of 0.0080 mg/l. Alternatively, the table indicates that a 45 percent decrease in the median concentration accompanied by a 60 percent decrease in the effluent variation also complies 95 percent of the time.

space

This example illustrated the effect of the magnitude of the variance on the rate of compliance for a continuous discharge. The existing condition mean effluent concentration of 0.0148 mg/l and mean effluent flow rate of 0.315 m^3/s, combine for a load rate of 0.403 kg/day. Reducing the concentration in the effluent by 40 percent reduces the load by 40 percent to 0.221 kg/day, while a reduction of 55 percent reduces the daily load to 0.181 kg/day. Clearly, by mixing the effluent in a retention tank or pond in order to discharge a less variable effluent compliance is possible for larger load rates. This analysis shows the importance, in some circumstances, of considering the level of variability of the effluent concentration when setting effluent limits.

TABLE 5.5: Percent Non-Compliance for Hypothetical Substance

Percent Decrease in median	Percent Decrease in Variance Effluent Concentration 0	20	40	60	80
0	36.5				
20	26.5				
40	11.7	9.2	8.2	6.7	5.0 *
45	11.1	7.8	7.0	5.5	2.9 *
50	10.2	5.4	3.5 *	2.8 *	0.9 *
55	4.9 *	2.7 *	2.1 *	1.2 *	0.5 *
60	2.4 *	1.8 *	0.6 *	0.1 *	0.0 *
- an asterix (*) indicates compliance					

6.0 CONCLUSIONS AND RECOMMENDATIONS

The water quality component of the Grand River MISA Pilot Site Study has been completed with respect to the objectives and goals of the MISA initiative, specifically, the setting of effluent limits for the Waterloo STP and demonstration of the methodology used to do so. Milestones in the development process are important enough on their own to be considered secondary goals. These secondary goals were screening for toxic organic parameters, qualitative and quantitative assessment of the ambient water quality, and impact assessment of the STP.

This report has outlined the methods of the sampling survey, the statistical description of the sample data as well presenting inferences about the sample populations of interest in a water quality survey. This section discusses the effectiveness of the sampling survey in fulfilling these requirements and makes recommendations for future surveys. The first stage in the analysis of the instream sample data was the non-parametric graphical presentation in the Box and Whisker plots. This visual tool demonstrates, in a qualitative way, the levels of parameter concentrations instream as well as the relative impact of loadings from the STP. This primary aspect was examined more rigorously and quantitatively using the Kruskal-Wallis statistical test to determine if the sampling program was able to demonstrate a significant impact due to the STP effluent. Eleven parameters were shown to have significantly higher concentrations downstream of the STP outfall than in the background upstream of the outfall. They were sodium, chloride, fluoride, filtered residue, strontium, conductivity, zinc, hardness, potassium, magnesium and pH. Nineteen parameters showed no significant difference.

The sampling results indicated that many of the parameters had low frequency of detection or were not detected at all. This subset of parameters included all the organic contaminants as well as some of the trace metals. These parameters can be viewed in the context

of screening only. The ones that were not detected can be considered indeterminant and the parameters detected rarely are considered present but with unknown mean and variance.

The investigation of the effects of the WPCP effluent on the Grand River water quality would be incomplete without consideration of concentration levels and discharge rate of the effluent. Two complimentary studies were available to supply some of this information. This data, where appropriate, was used in the modelling process undertaken in this study. The sampling program supplied data in sufficient detail to estimate cross-stream average concentrations for instream quality independant of season, precipitation events or daily cycles. The most detailed model that can be used within the constraints of available data was the Monte Carlo simulation model and its utility was demonstrated in this report.

The results indicate that, for the trace metal and conventional parameters, there was a low to moderate impact from the STP on the Grand River water quality. These parameters have been ranked according to their relative frequency of exceedence of PWQOs for parameters with a PWQO. The data from sampling for organic parameters is in a presence/absence format and 21 parameters from the EMPPL subset of 126 parameters were detected in the Grand River. Lindane (BHC-gamma) was the most prevalent organic parameter detected in the water column. The modelling results for the trace metals lead, zinc and copper showed that the Waterloo STP's contribution to the rate of non-compliance was relatively small. The median effluent concentration for phosphorus should be reduced from 1.027 mg/l to 0.0792 mg/l to ensure compliance with Policy 2 in the "Blue Book" (OME, 1984).

The study reach selected was too long and there were too many sampling stations. Less bias in the data, lowered expenses and ease of interpretation could have been accomplished by sampling at one station immediately upstream of the outfall and one or two

stations downstream. This would allow for more intensive sampling for the same expenditure. Sampling should be designed to accomplish more objectives for each sampling outing.
By spreading the sampling across river transects a cross-stream average could have been used to eliminate spatial bias in the data as well as providing inputs to a mixing zone model. There were no QA/QC methods applied at the sampling level used in this study, thus not allowing an estimate or error contributions to the variance of the results to be made.

The added feature of fewer stations and a smaller study reach would be the ability to assess the STP impact alone without having to consider the complication of the other contaminant inputs to the Study area.

There was a large list of parameters tested for in the instream water column and a much smaller list of parameters tested for in the effluent. Modelling could only be performed for parameters tested in both, hence the ability to assess the STP's contribution to reduced water quality in the Grand River for most of the parameters of concern was lost.

Flow data from the Grand River Conservation Authority stream flow gauge at the Bridgeport Bridge was used for this study. The data had to be corrected to account for ice conditions. An estimate of low flows in the study area is therefore of unknown reliability. Sources of hydrological data should be analysed for applicability before the sampling survey is started. The combination of reliable flow data and concentrations will allow correlation estimates between these two parameters. An important aspect of river water quality assessment.

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Watershed Management Section

APPENDIX A

LIST OF SAMPLING PARAMETERS

CONVENTIONALS

Alkalinity
Ammonium
Calcium
Chloride
Conductivity
Dissolved Organic Carbon
Fluoride
Hardness
Magnesium
Nitrate
Nitrite
pH
Phosphorus, filtered
Phosphorus, total
Potassium
Residue, Filtrate
Residue, Particulate
Sodium
Total Kjeldahl Nitrogen

TRACE METALS

Aluminum
Arsenic
Barium
Boron
Beryllium
Cadmium
Cobalt
Cyanide, free
Cyanide, available
Chromium
Copper
Iron
Manganese
Mercury
Nickel
Lead
Selenium
Silver
Strontium
Vanadium
Zinc

ORGANICS

1,1-dichloroethylene
Chloroform
Tetrachloroethylene
Toluene
1,1,1-trichloroethane
Hexadecanotic Acid
Ethyl Benzene
M&P-Xylene
O-xylene
Butoxyethoxyethanol
Dichloromethane
Trans-1,2-dichloroethylene
Dichloroethane
1,2-dichlorethane
Carbon Tetrachloride
1,2-dichloropropane
Trichloroethylene
Dichlorobromomethane
1,1,2-trichlorethane
Chlorodibromomethane
Bromoform
1,1,2,2-tetrachloroethane
Hexachloroethane
Hexachlorobutadiene
Hexachlorocyclopentadiene
Trifluorchlorotoluene
Nitrobenzene
1,1-dichloroethane
1-methylnapthalene
~~Bromodichloromethane~~
Ethylene Dibromode
1,4-dichlorobenzene
1,3-dichlorobenzene
1,2-dichlorobenzene
1,2,4-trichlorobenzene
2,3,6-trichlorotoluene
2,4,5-trichlorotoluene
2,6,A-trichlorotoluene
Chlorobenzene
1,2,3-trichlorobenzene
1,2,3,4-tetrachlorobenzene
1,2,3,5-tetrachlorobenzene
1,2,4,5-tetrachlorobenzene
1,3,5-trichlorobenzene
2,3,4,5-tretrachlorophenol
2,3,5,6-tretrachlorophenol
2-chlorophenol
2,4-dichlorophenol
2,4,6-trichlorophenol
2,3,4-trichlorophenol
2,4,5-trichlorophenol
2,3,4,6-tetrachlorophenol
2,3-dichlorophenol

ORGANICS (continued)

Hexachlorobenzene
Pentachlorobenzene
Pentachlorophenol
Trihalomethanes Total
2,4-dichlorophenoxyacetic Acid
2,4-dichlorophenoxybutyric Acid
2,4,5-trichlorophenoxyacetic Acid
2,4-dinitrophenol
Lindane (BHC-Gamma)
PP-DDT
Aldrin
BHC Alpha
BHC Beta
Chlordane-Alpha
Chlordane-Gamma
Dieldrin
Oxychlordane
OP-DDT
PCB Total
PP-DDD
PP-DDE
Toxaphene
Aminocarb
Bux
Carbofuran
CIPC
Diallate
Eptam
Propoxur
Sevin
Sutan
Parathion
Endrin
Endosulfan Sulfate
Endosulfan I
Endosulfan II
Heptachlorepoxide
Heptachlor
Mirex
Diazinon
Dichlorvos
Dursban
Ethion
Guthion
Malathion
Mevinphos
Methyl Parathion
Methyl Trithion
Reldan
Ronnel
Phorate (Thimet)
Dicamba
Silvex

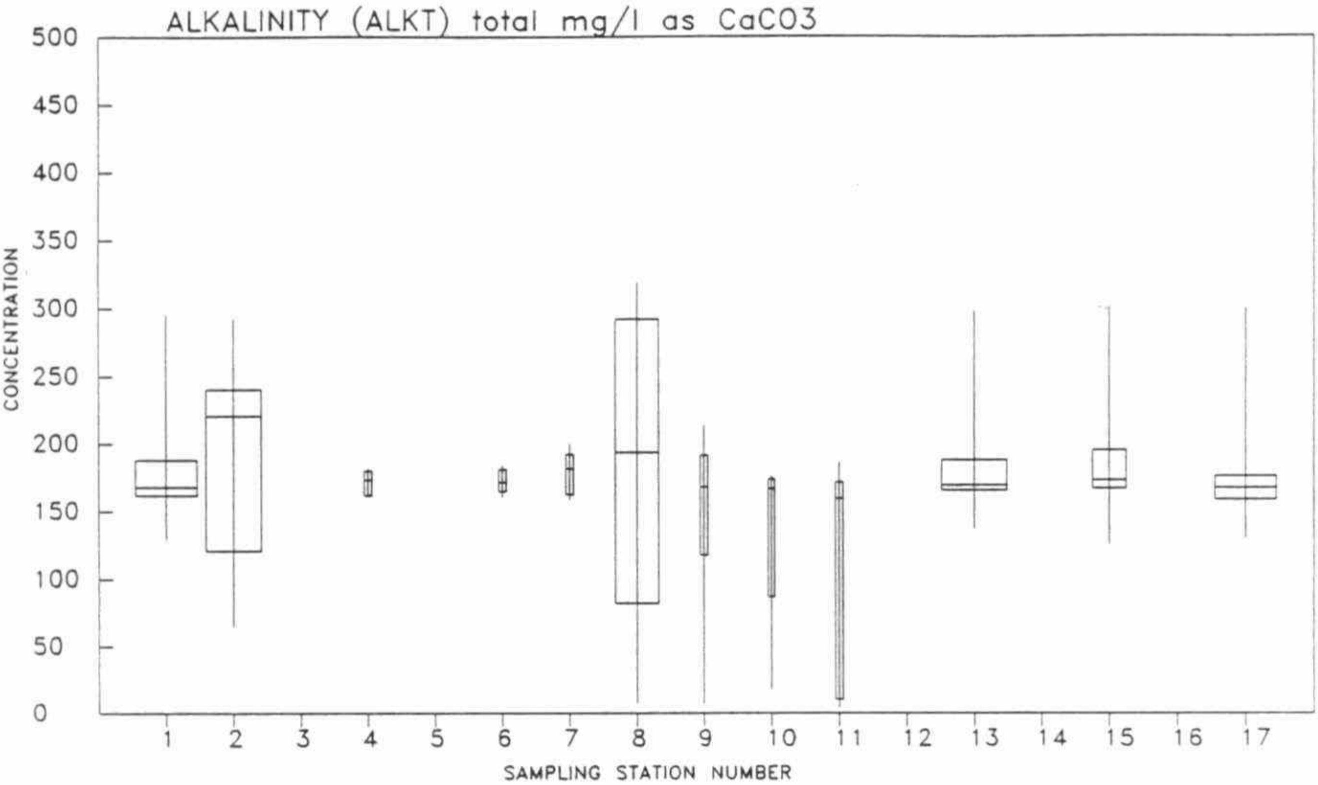
ORGANICS (continued)

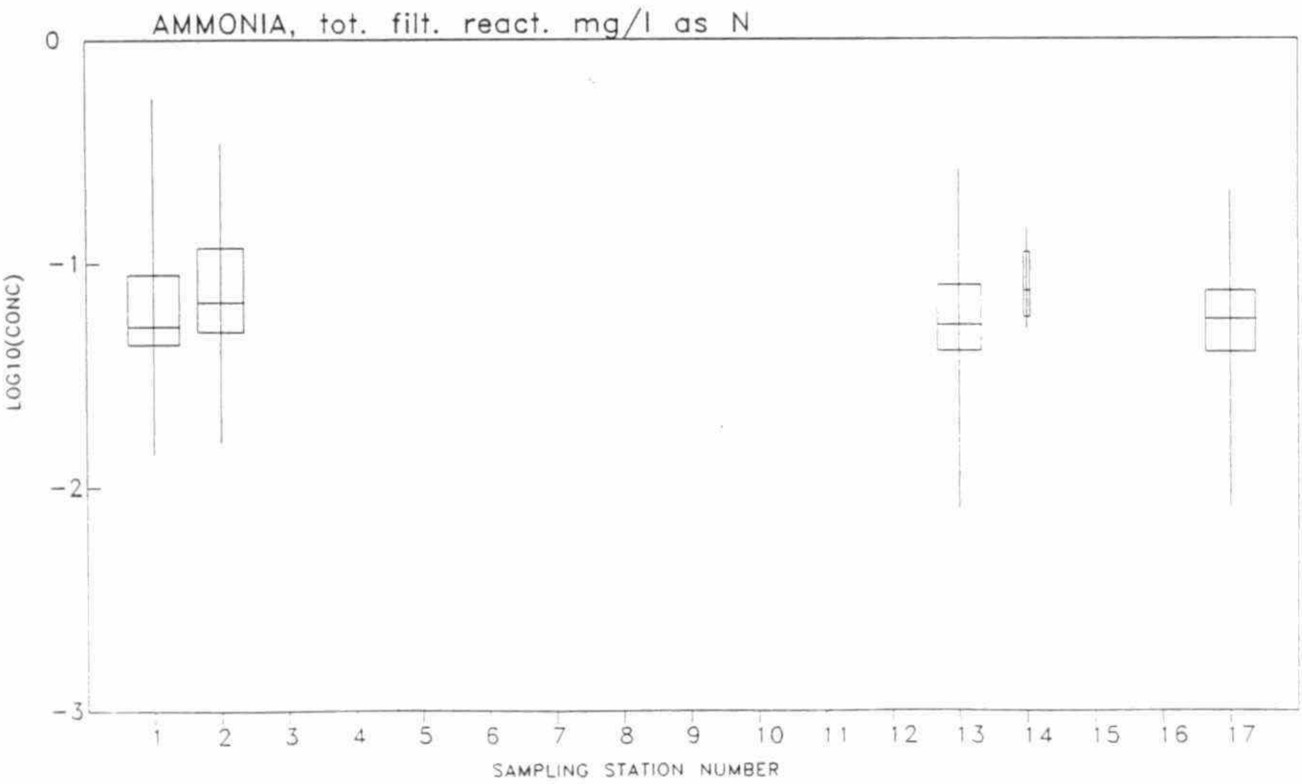
Pichloram
Di-N-Butylphthalate
Bis(2-ethylhexyl)phthalate
Phenanthrene
Di-T Butylmethylphenol
4-bromophenylphenylether
Dimethylphthalte
Diethylphthalte
Di-N Octylphthalte
Bis(2-chloroethoxy)methane
p-chloroaniline
2-chloronaphthalene
Octachlorostyrene
n-nitrosodimethylamine
n-nitrosodipropylamine
1,2-diphenylhydrazine
Caffeine
4-chlorophenylphenylether
Bis(2-chloroisopropyl)ether
Bis(2-chloromethyl)ether
Di-isobutyl Phthalate
N-nitrosodiphenylamine
Phenol
2,4-dimethylphenol
p-chloro-m-cresol
2,6-dinitrotoluene
2,4-dinitrotoluene
2-nitrophenol
4-nitrophenol
4,6-dinitro-o-cresol
Anthracene
Fluoranthene
Pyrene
Benz(a)anthracene
Chrysene
Benzo(b)fluoranthene
Benzo(k)fluoranthene
Benzo(a)pyrene
Benzo(g,h,i)perylene
Dibenz(a,h)anthracene
Acenaphthylene
Acenaphthene
Fluorene
IPC
Benzene
Naphthalene
Benzylbutylphthalte
Benzothiazole
Butyl Benzylphthalate
Indeno(1,2,3-cd)pyrene
Benonyl
2-chloroethylvinylether

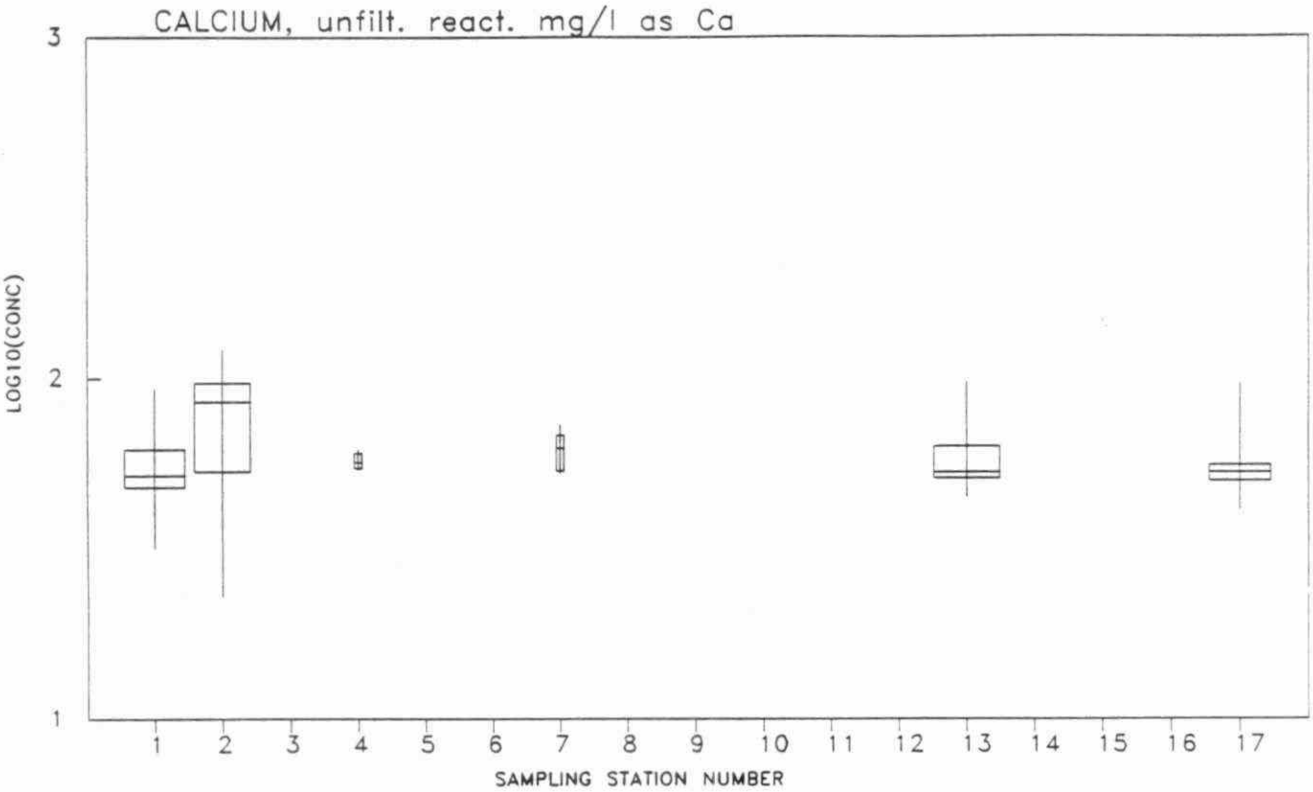
APPENDIX B

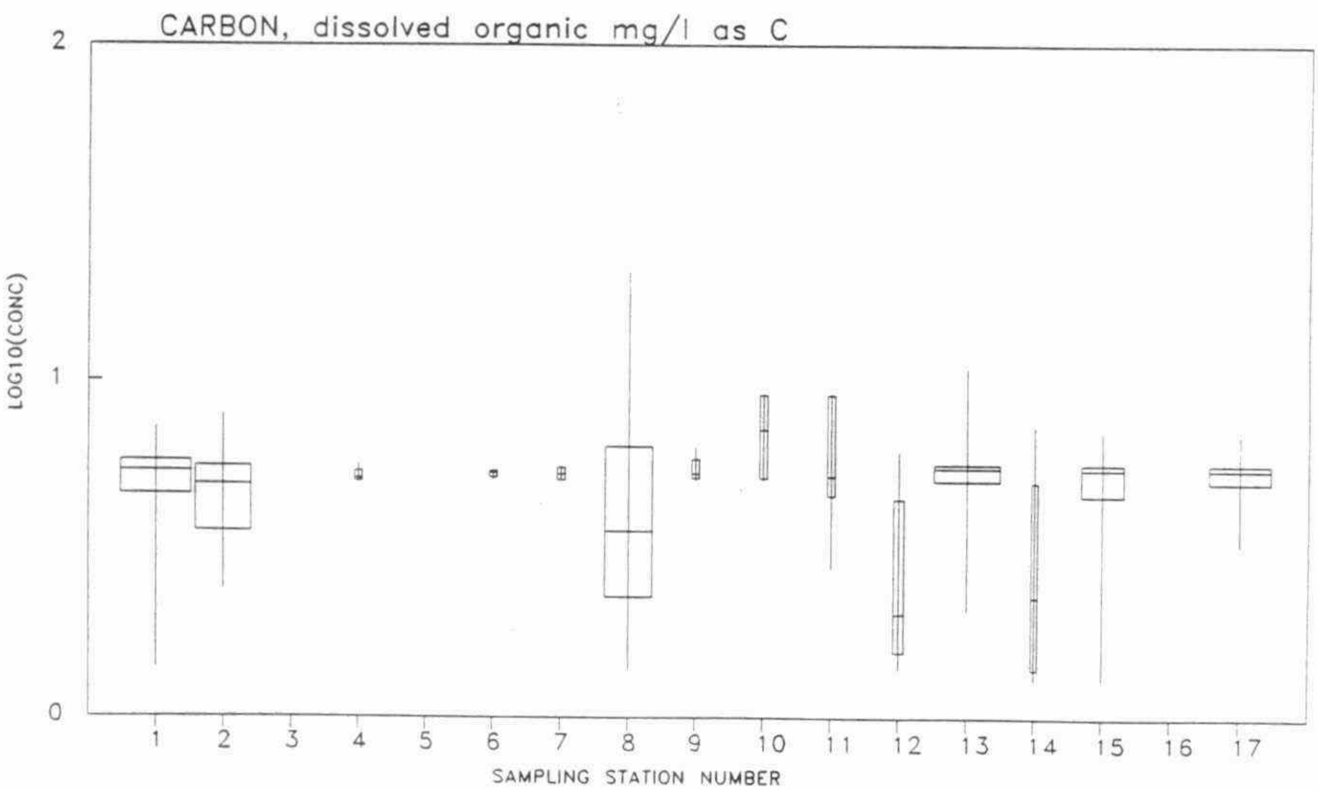
BOX AND WHISKER PLOTS

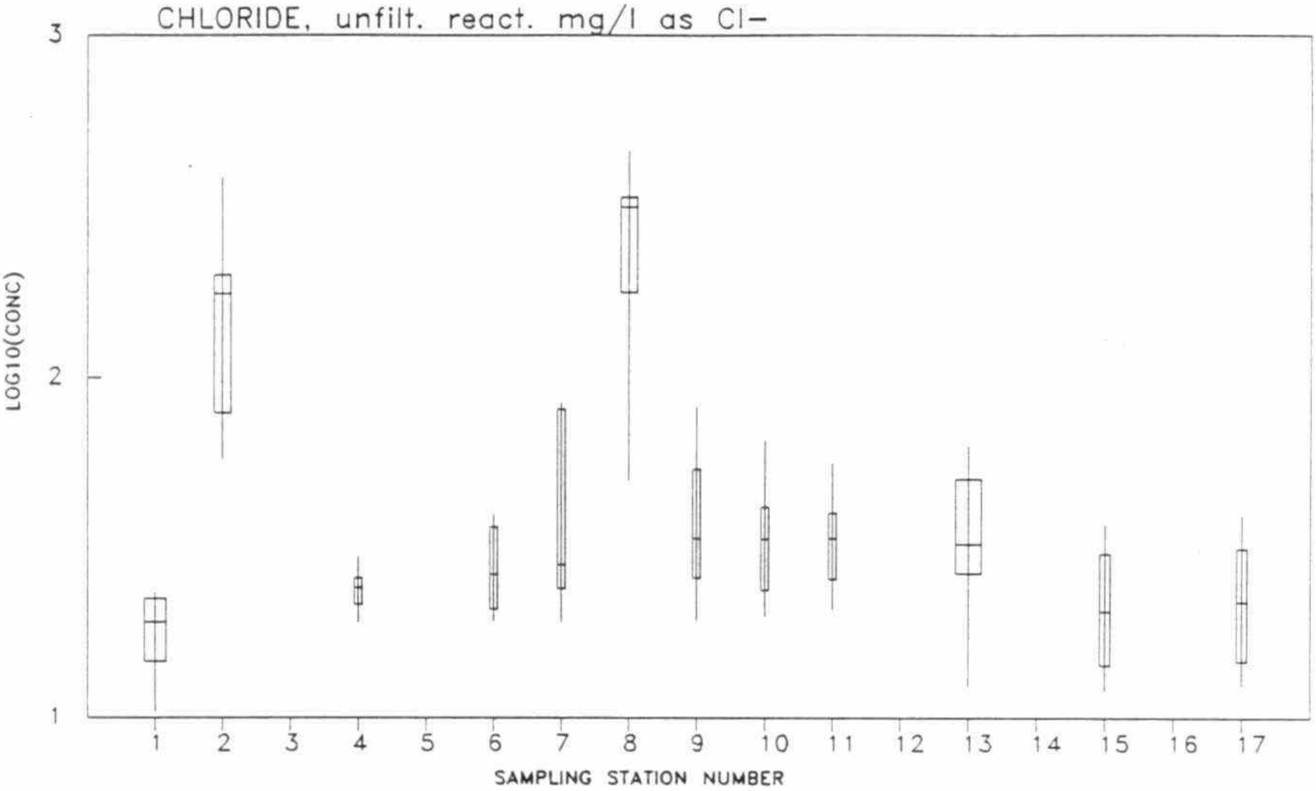
OF SAMPLE DATA


ALKALINITY (ALKT) total mg/l as CaCO3
CONCENTRATION
500
450
400
350
300
250
200
150
100
50
0
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17
SAMPLING STATION NUMBER

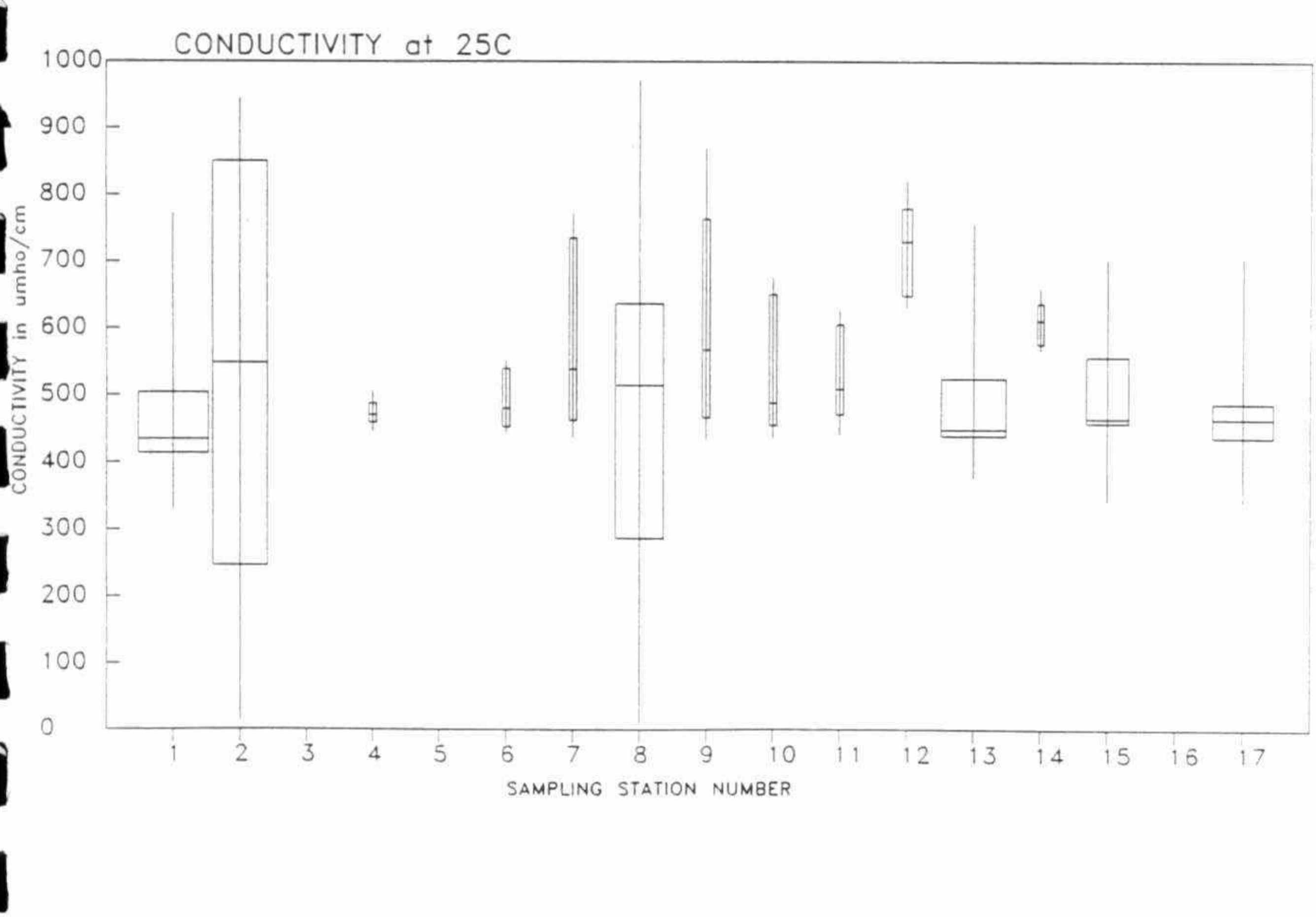

AMMONIA, tot. filt. react. mg/l as N
LOG10(CONC)
0
-1
-2
-3
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17
SAMPLING STATION NUMBER


CALCIUM, unfilt. react. mg/l as Ca
LOG10(CONC)
3
2
1
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17
SAMPLING STATION NUMBER

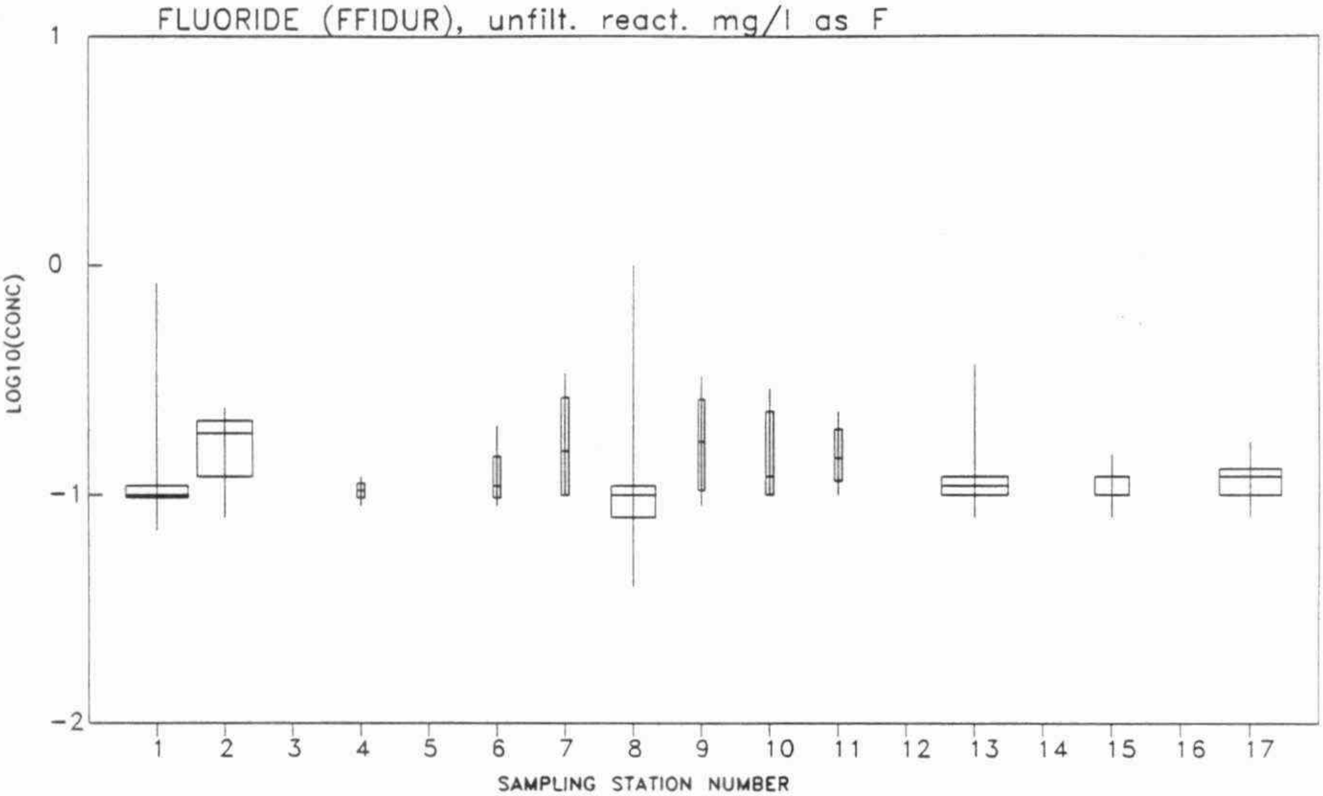

CARBON, dissolved organic mg/l as C
LOG10(CONC)
2
1
0
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17
SAMPLING STATION NUMBER



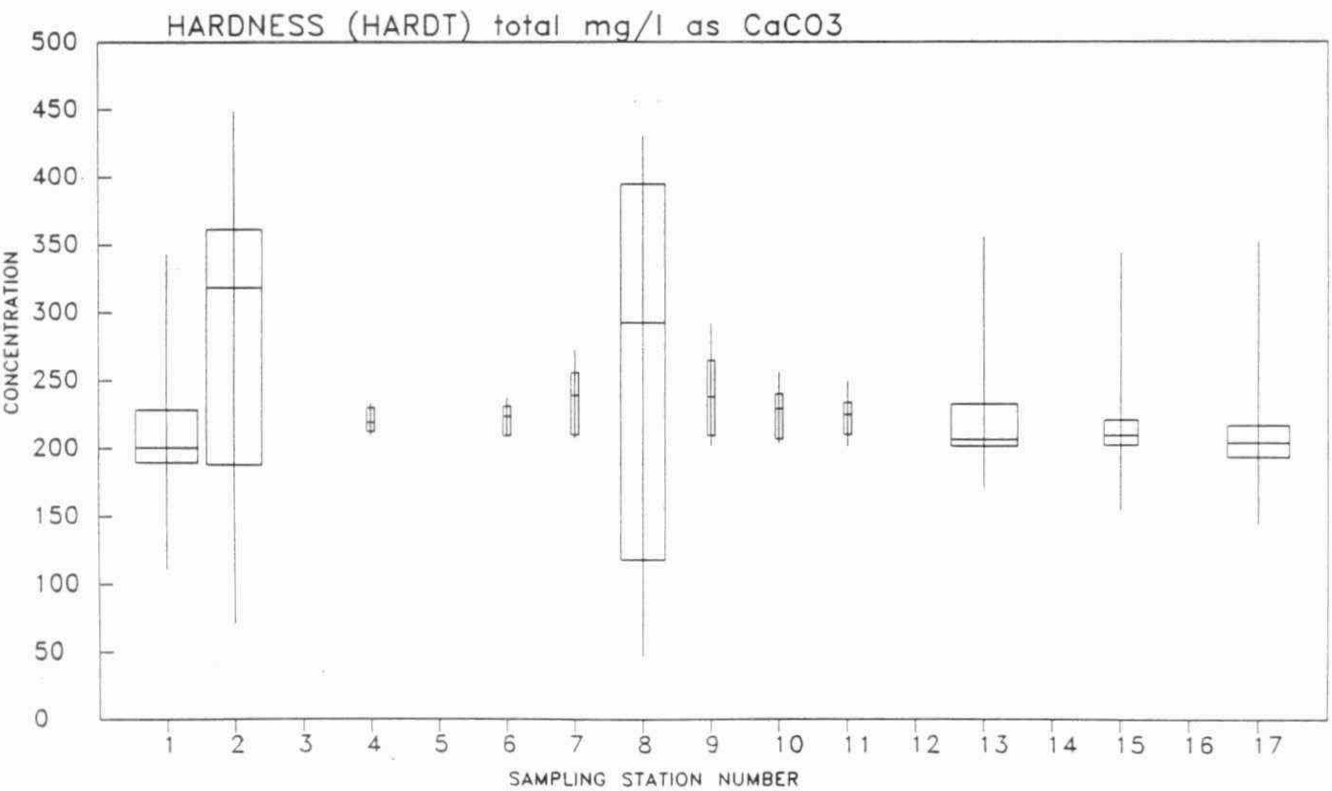
CHLORIDE, unfilt. react. mg/l as Cl−
LOG10(CONC)
3
2
1
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17
SAMPLING STATION NUMBER



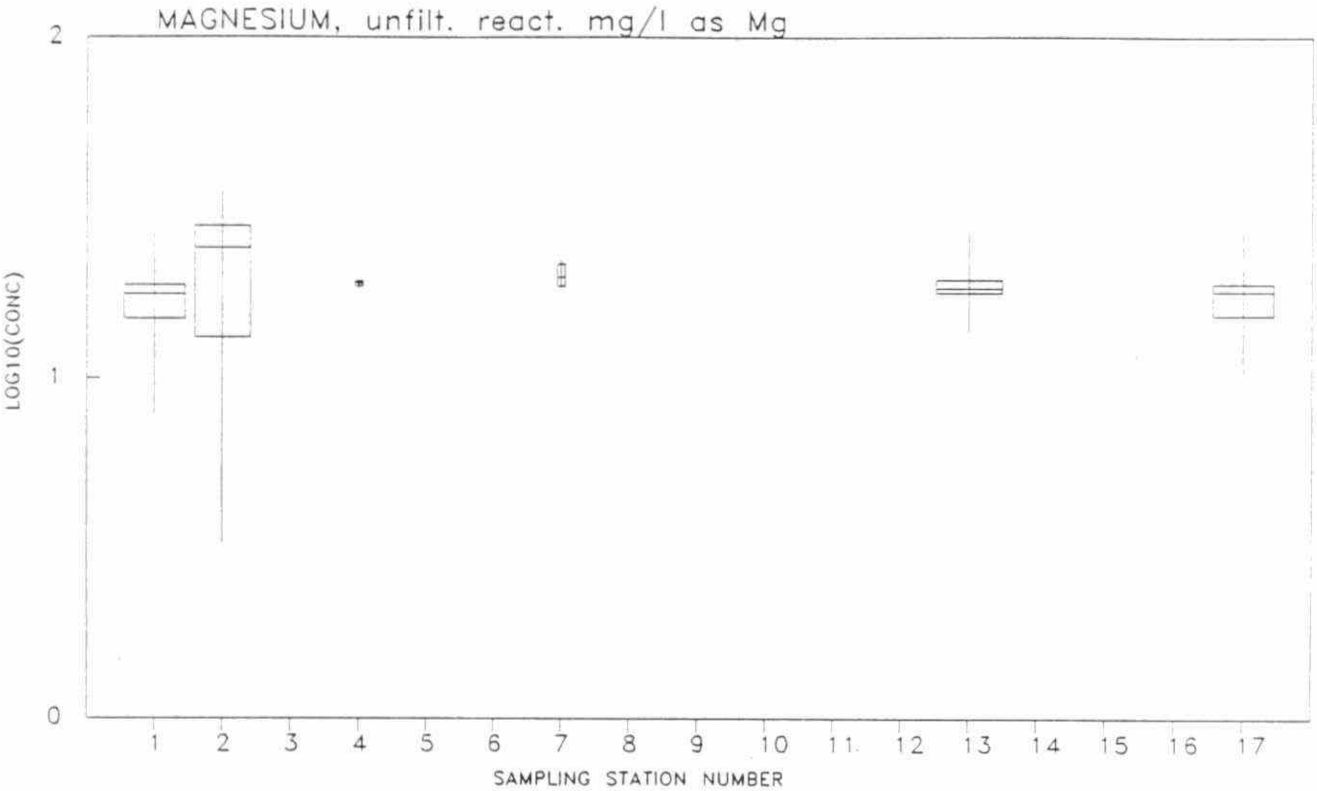
CONDUCTIVITY at 25C
CONDUCTIVITY in umho/cm
1000
900
800
700
600
500
400
300
200
100
0
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17
SAMPLING STATION NUMBER



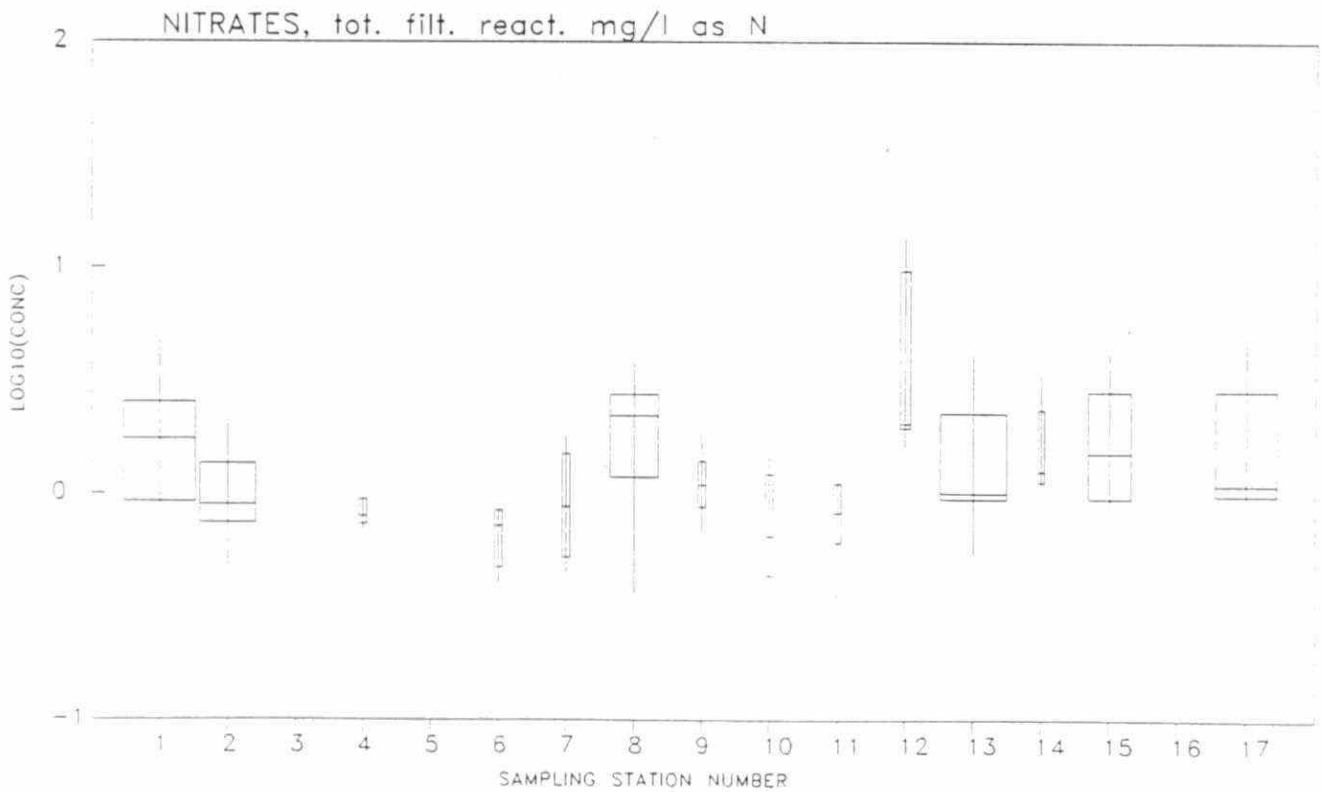
FLUORIDE (FFIDUR), unfilt. react. mg/l as F
LOG10(CONC)
1
0
-1
-2
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17
SAMPLING STATION NUMBER



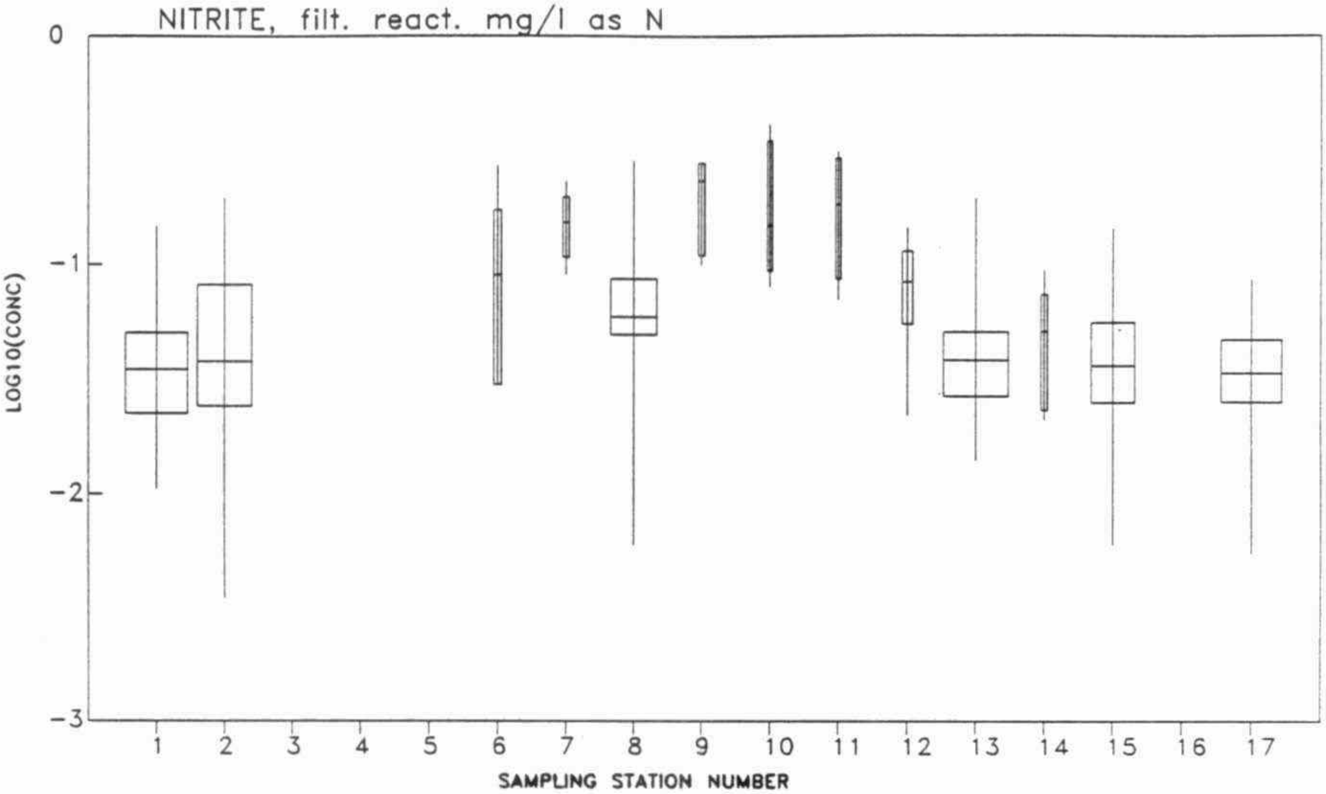
HARDNESS (HARDT) total mg/l as CaCO3
CONCENTRATION
500
450
400
350
300
250
200
150
100
50
0
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17
SAMPLING STATION NUMBER

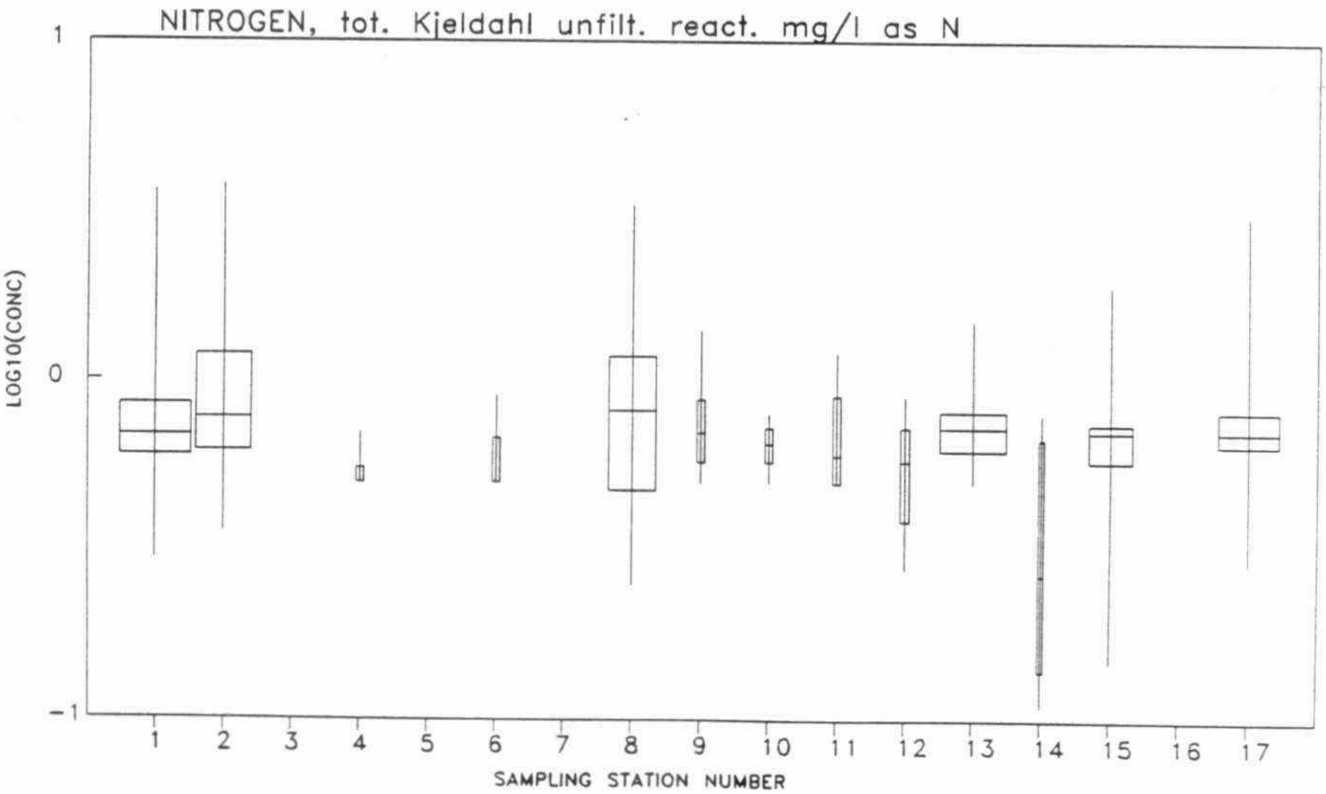


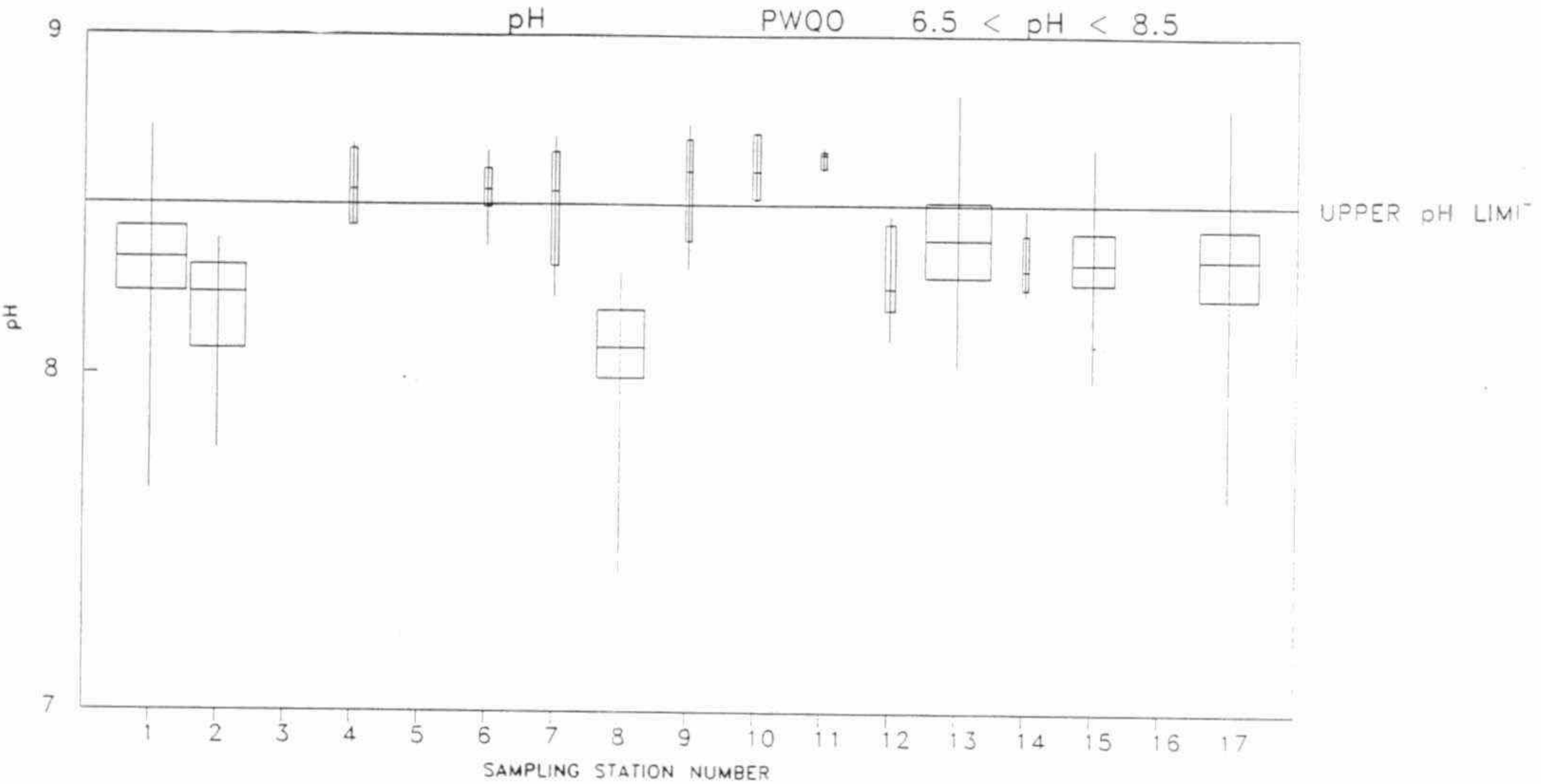
MAGNESIUM, unfilt. react. mg/l as Mg
LOG10(CONC)
2
1
0
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17
SAMPLING STATION NUMBER



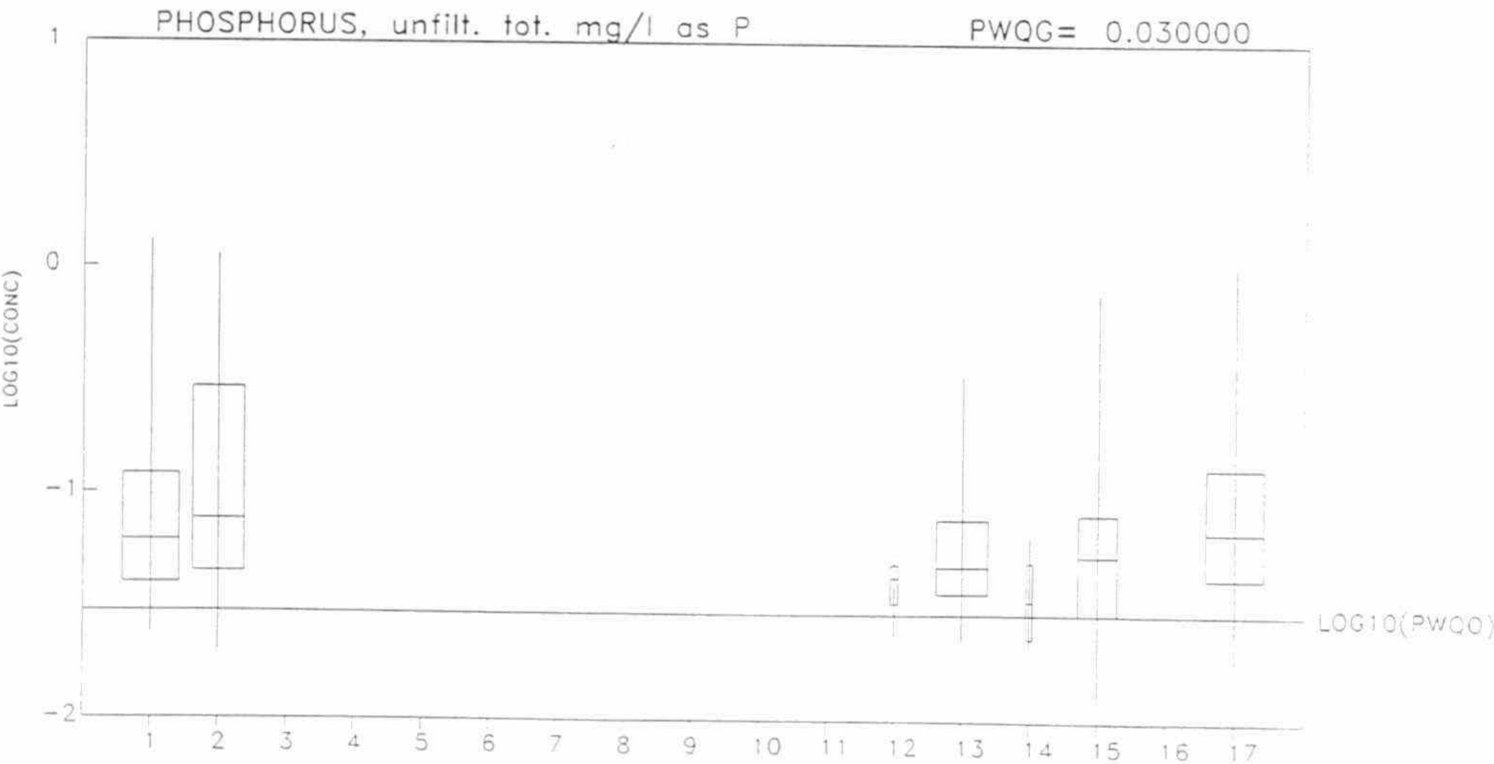
NITRATES, tot. filt. react. mg/l as N
LOG10(CONC)
2
1
0
-1
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17
SAMPLING STATION NUMBER


NITRITE, filt. react. mg/l as N
LOG10(CONC)
0
-1
-2
-3
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17
SAMPLING STATION NUMBER

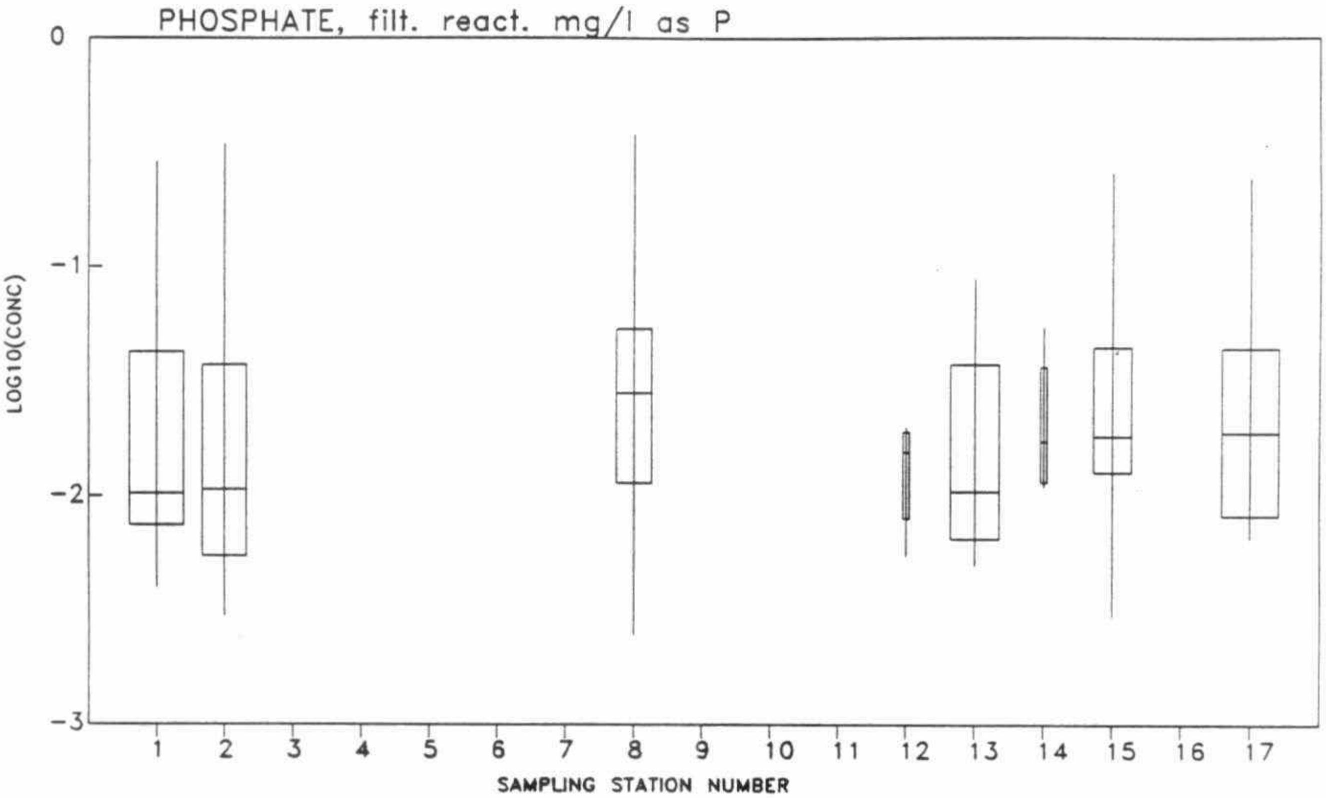

NITROGEN, tot. Kjeldahl unfilt. react. mg/l as N
LOG10(CONC)
1
0
-1
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17
SAMPLING STATION NUMBER

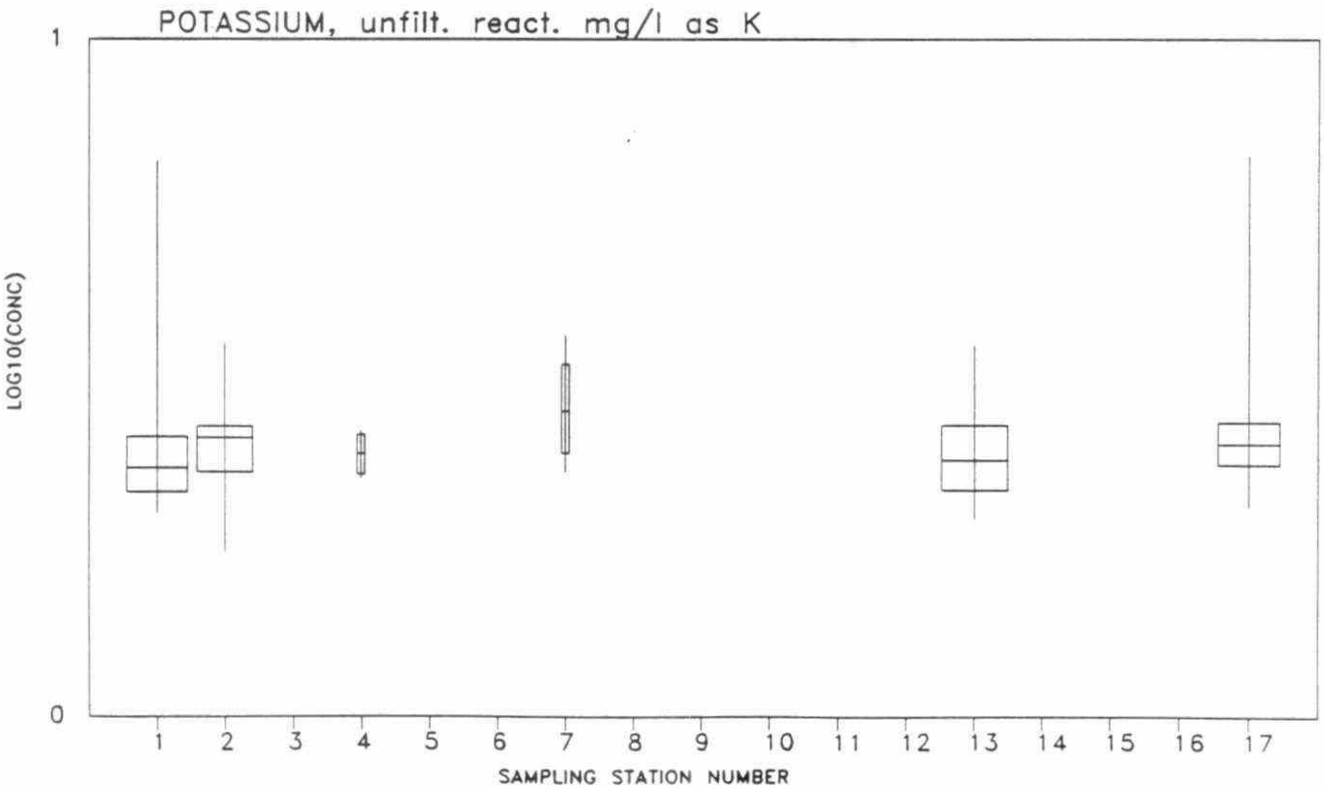


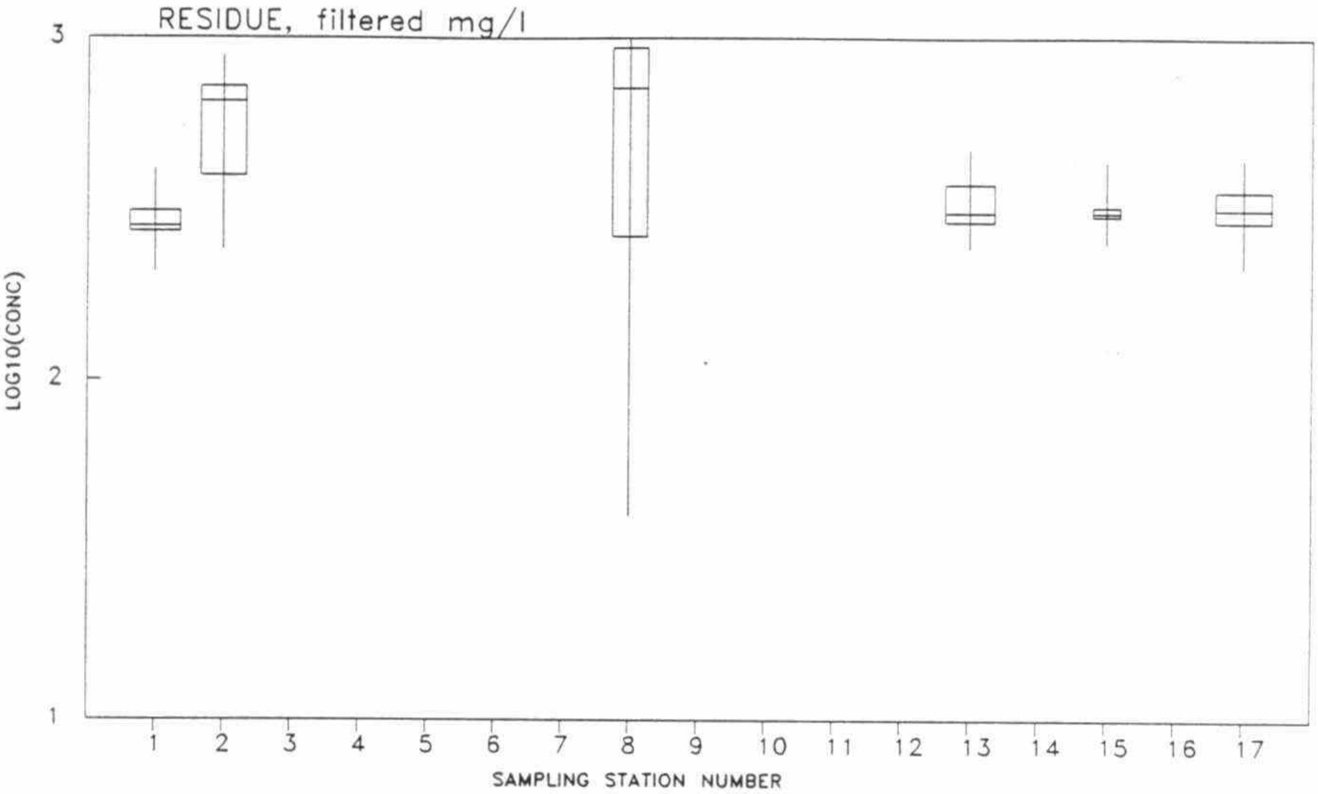
pH
PWQO 6.5 < pH < 8.5
9
8
7
pH
UPPER pH LIMIT
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17
SAMPLING STATION NUMBER

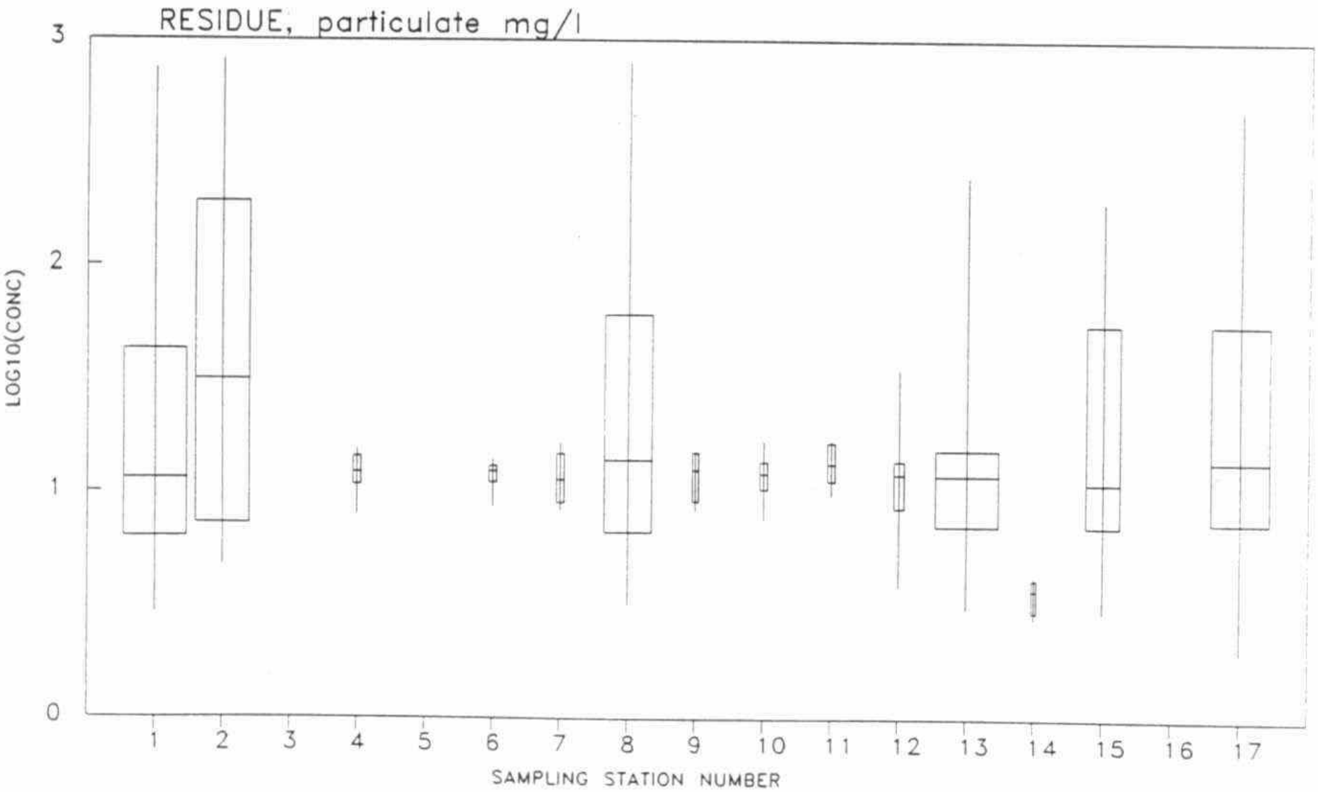


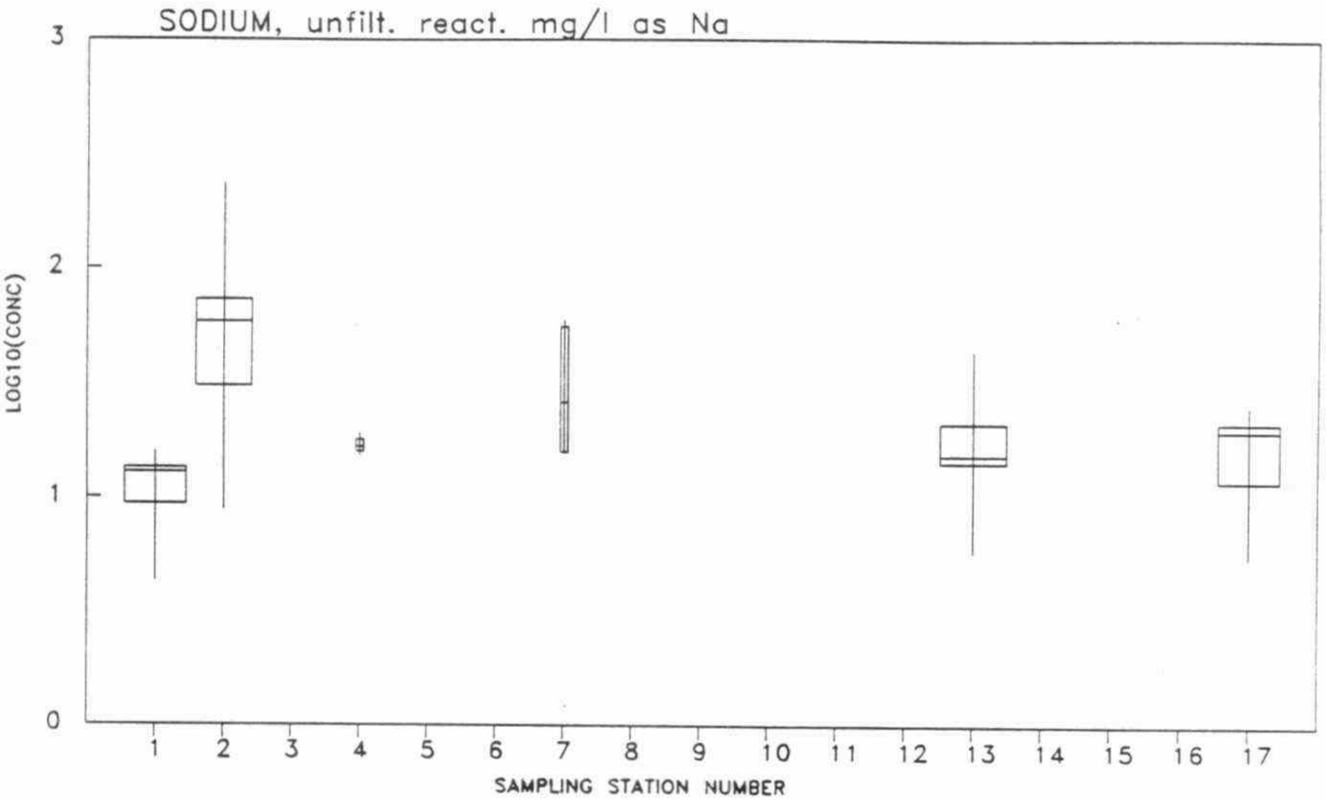
PHOSPHORUS, unfilt. tot. mg/l as P
PWQG= 0.030000
1
0
-1
-2
LOG10(CONC)
LOG10(PWQO)
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17
SAMPLING STATION NUMBER


PHOSPHATE, filt. react. mg/l as P
LOG10(CONC)
0
-1
-2
-3
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17
SAMPLING STATION NUMBER

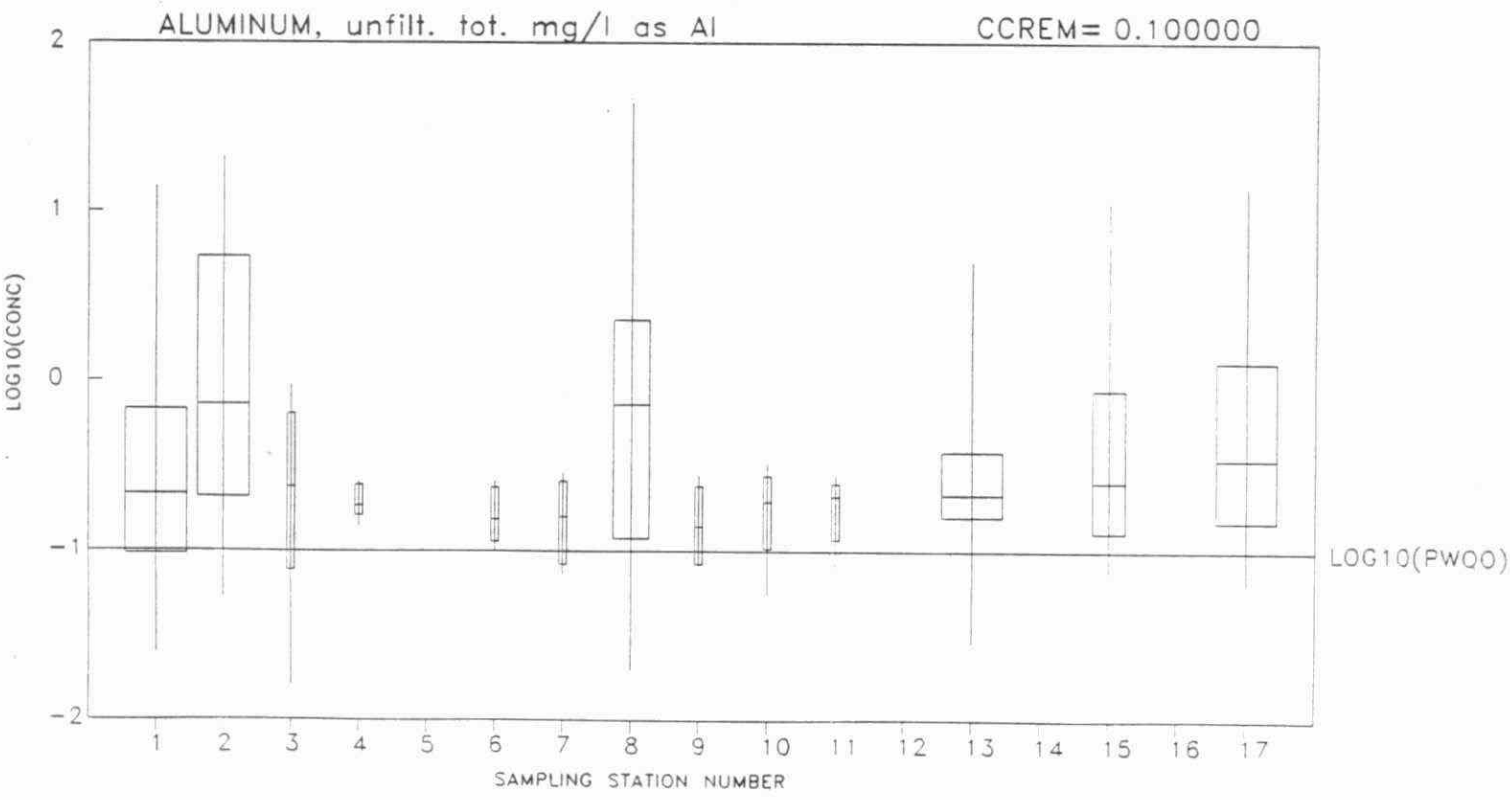

POTASSIUM, unfilt. react. mg/l as K
LOG10(CONC)
1
0
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17
SAMPLING STATION NUMBER


RESIDUE, filtered mg/l
LOG10(CONC)
3
2
1
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17
SAMPLING STATION NUMBER

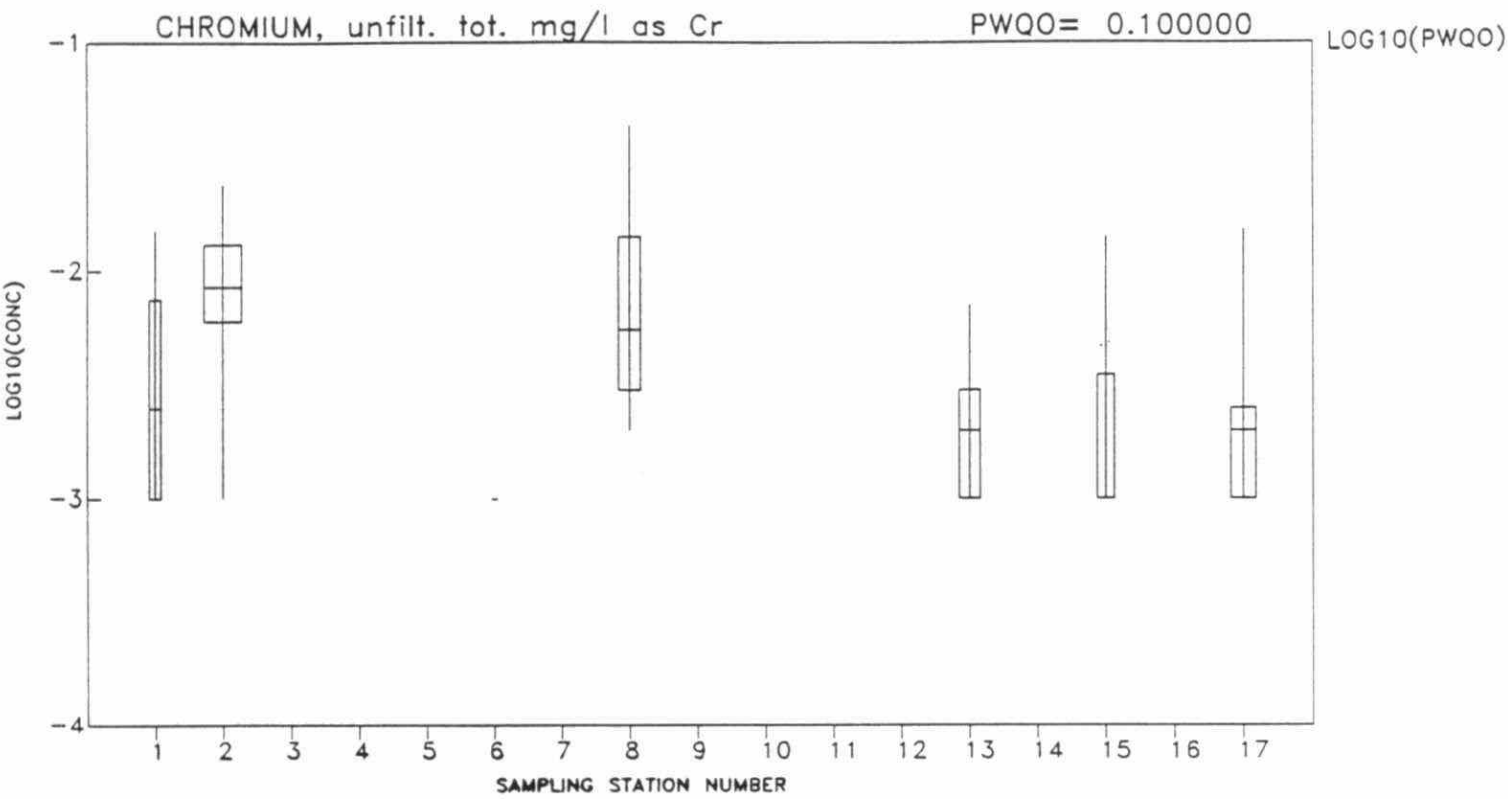

RESIDUE, particulate mg/l
LOG10(CONC)
3
2
1
0
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17
SAMPLING STATION NUMBER

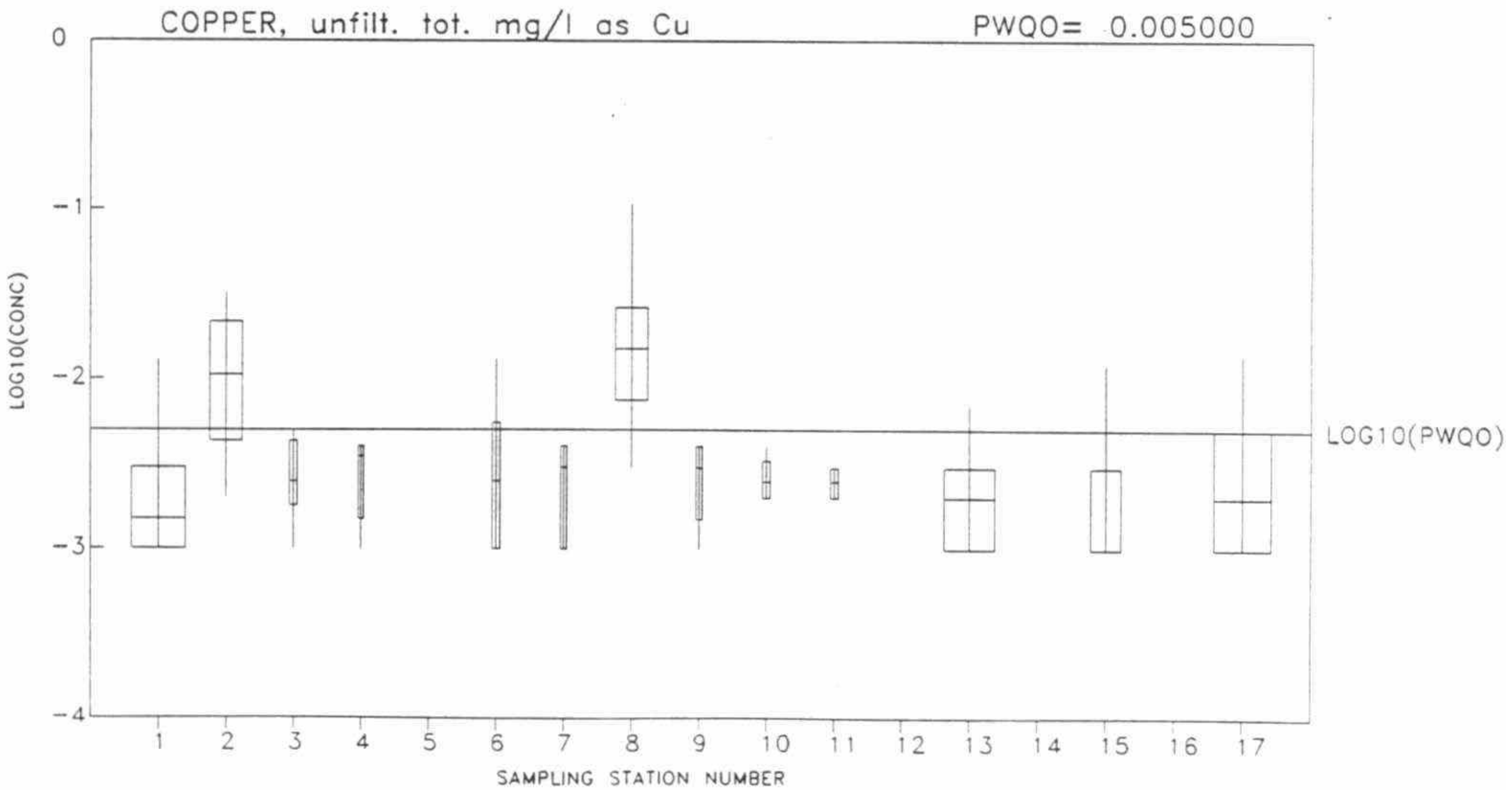


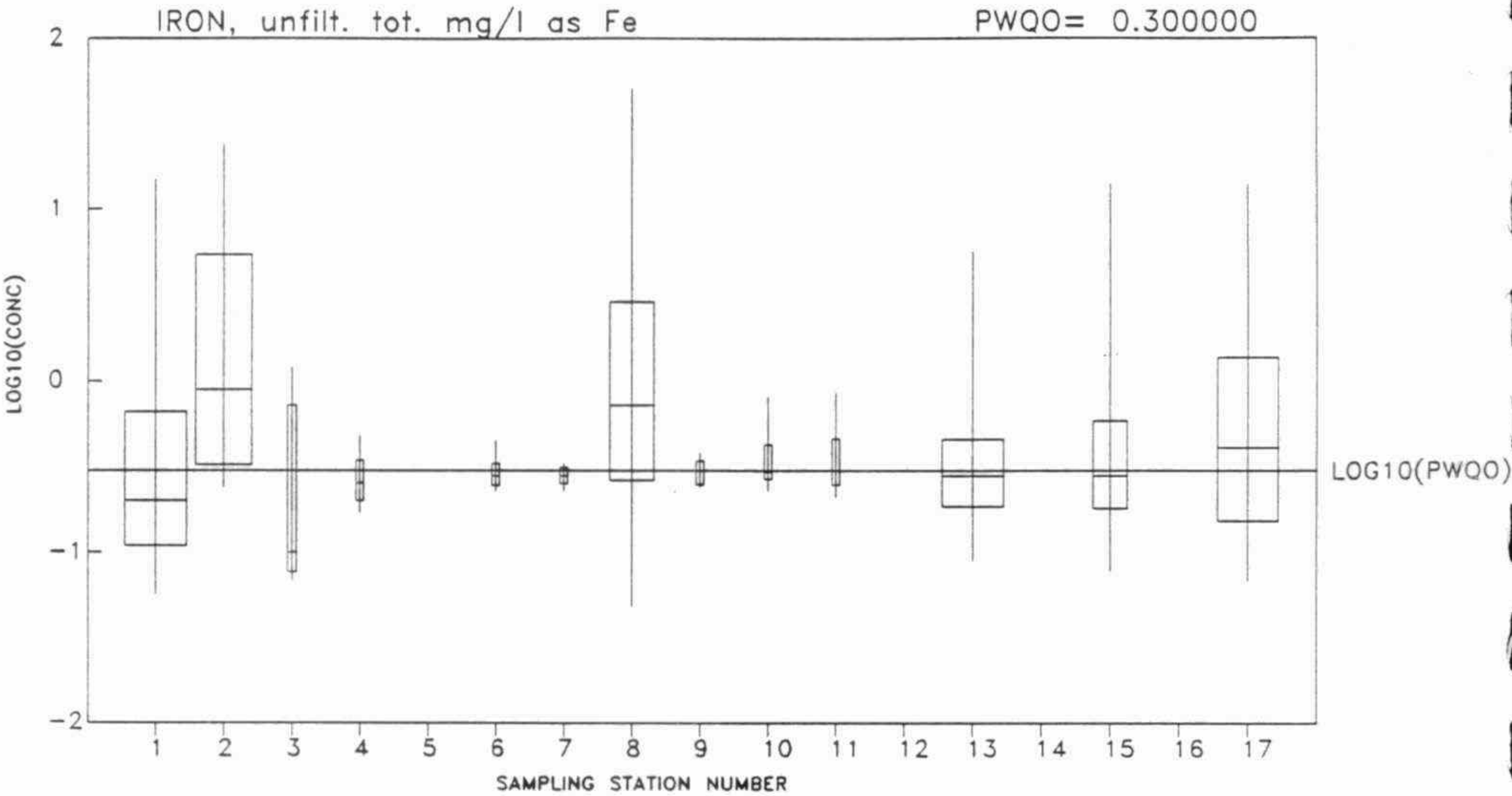
SODIUM, unfilt. react. mg/l as Na
LOG10(CONC)
3
2
1
0
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17
SAMPLING STATION NUMBER



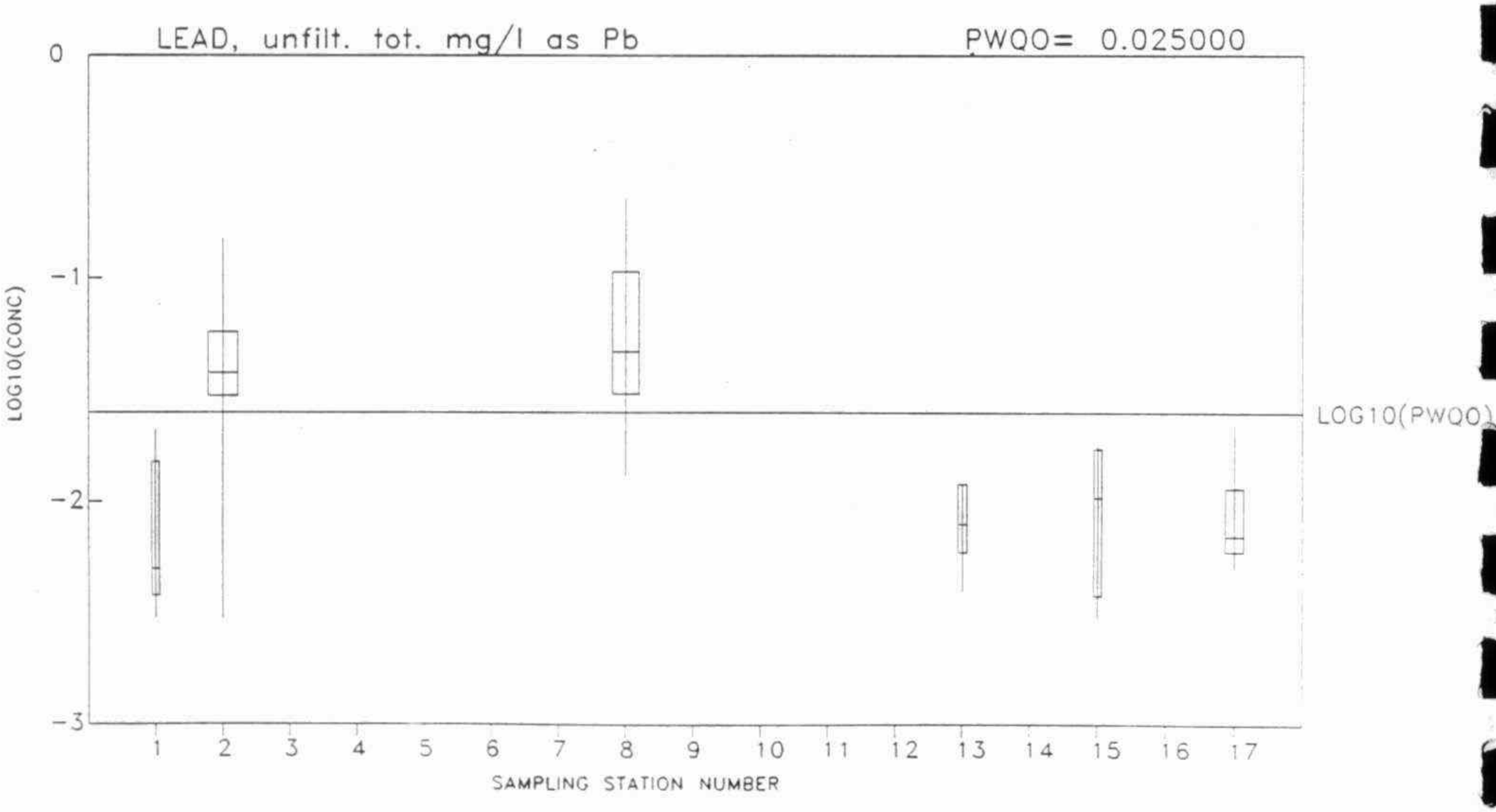
ALUMINUM, unfilt. tot. mg/l as Al
CCREM= 0.100000
LOG10(CONC)
2
1
0
-1
-2
LOG10(PWQO)
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17
SAMPLING STATION NUMBER


CHROMIUM, unfilt. tot. mg/l as Cr
PWQO= 0.100000
LOG10(PWQO)
LOG10(CONC)
-1
-2
-3
-4
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17
SAMPLING STATION NUMBER

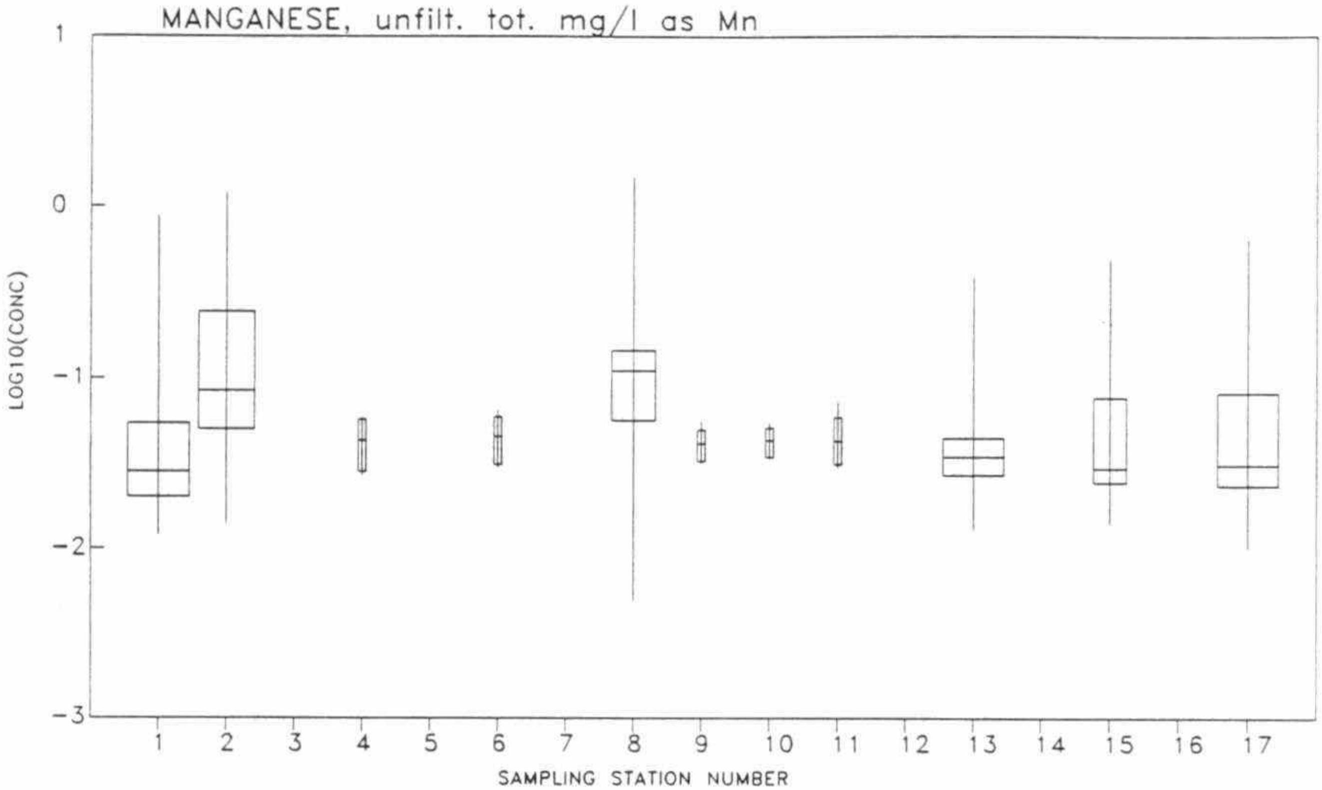

COPPER, unfilt. tot. mg/l as Cu
PWQO= 0.005000
LOG10(PWQO)
LOG10(CONC)
0
-1
-2
-3
-4
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17
SAMPLING STATION NUMBER

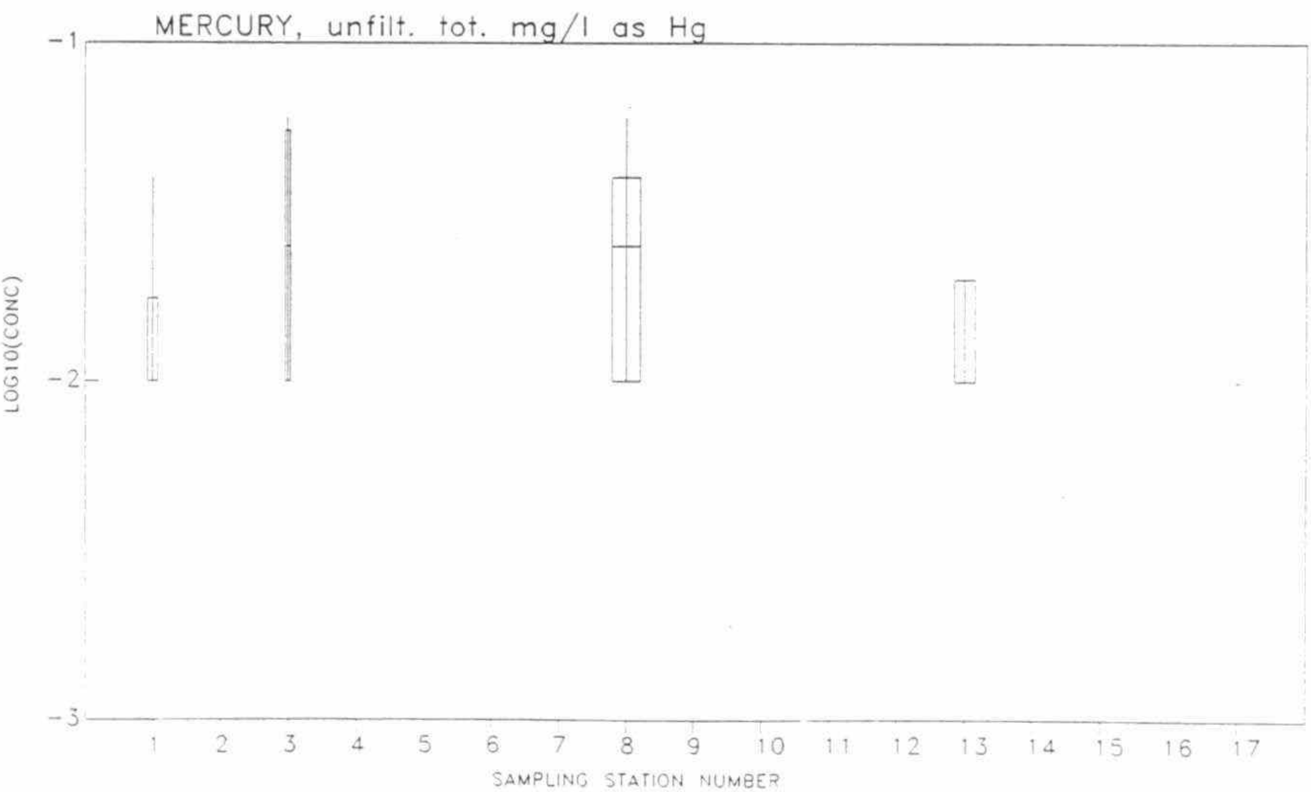


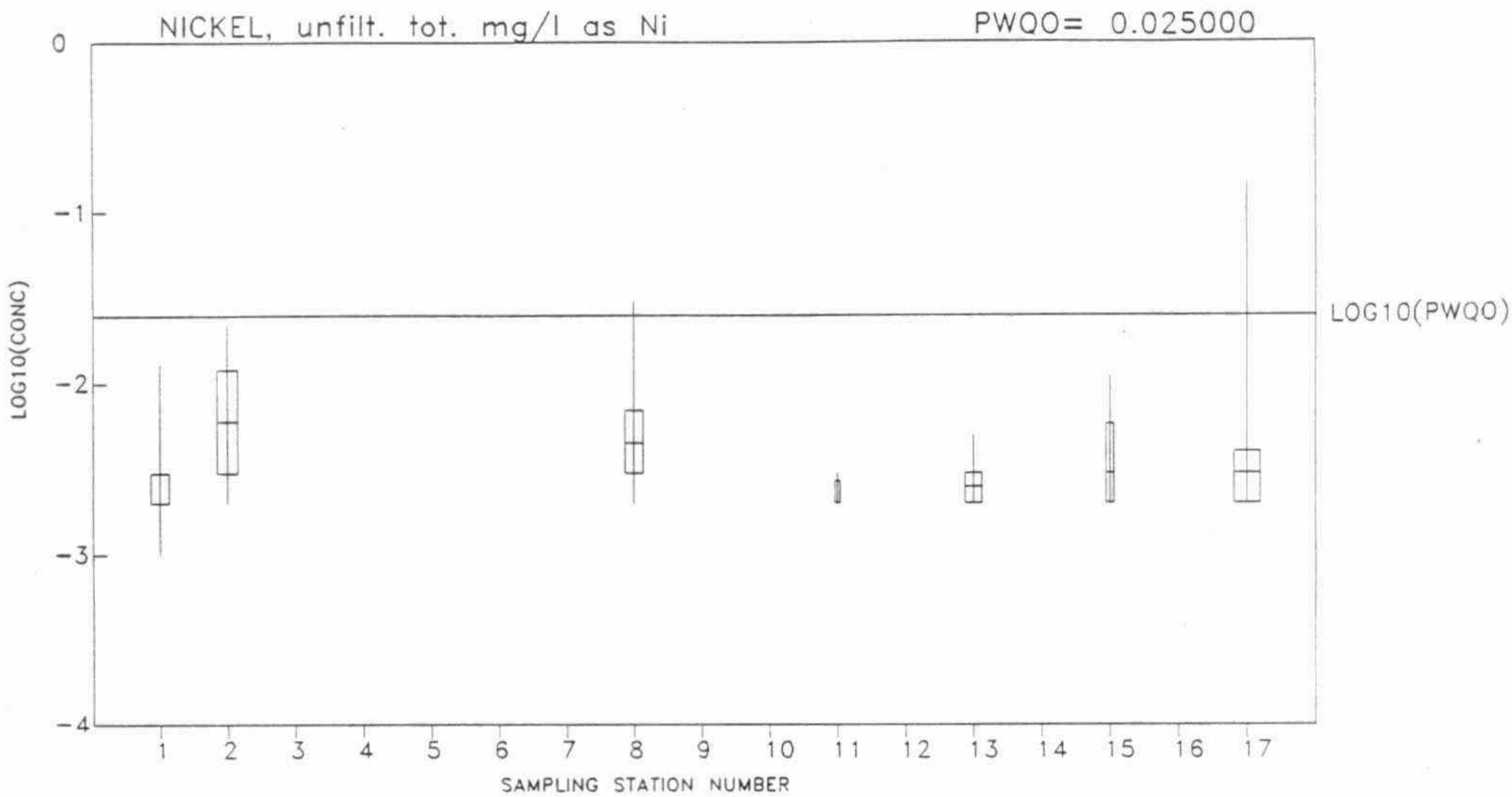
IRON, unfilt. tot. mg/l as Fe
PWQO= 0.300000
LOG10(CONC)
LOG10(PWQO)
SAMPLING STATION NUMBER

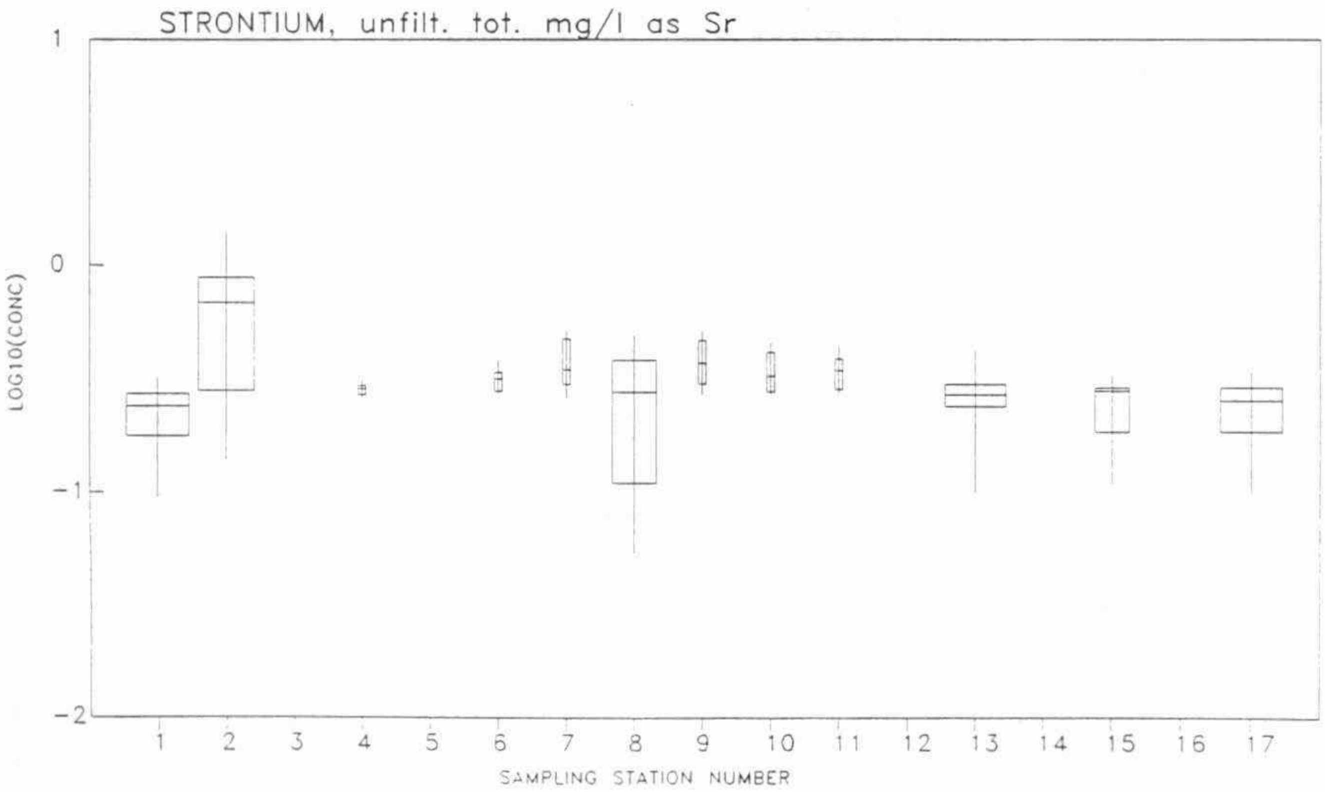


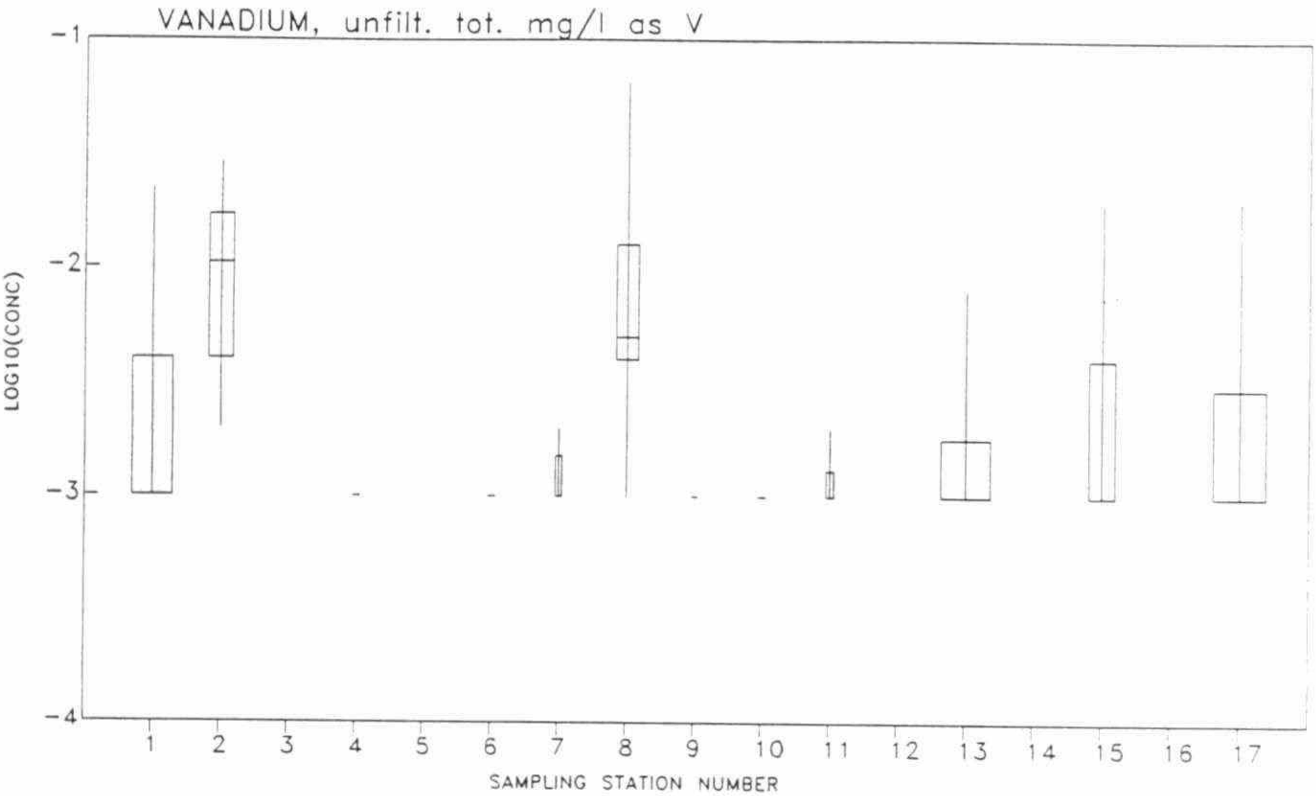
LEAD, unfilt. tot. mg/l as Pb
PWQO= 0.025000
LOG10(CONC)
LOG10(PWQO)
SAMPLING STATION NUMBER


MANGANESE, unfilt. tot. mg/l as Mn
1
0
-1
-2
-3
LOG10(CONC)
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17
SAMPLING STATION NUMBER

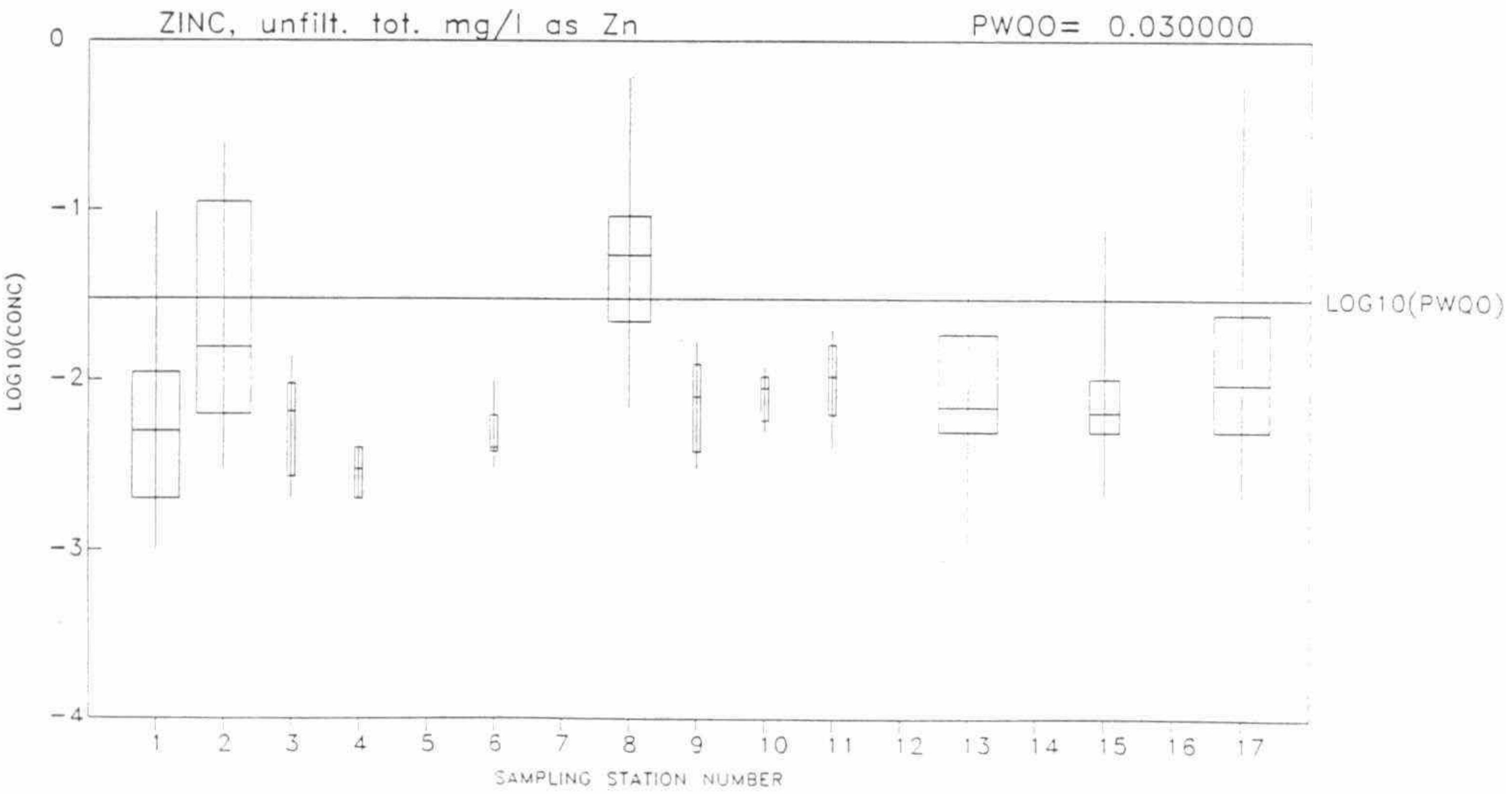

MERCURY, unfilt. tot. mg/l as Hg
-1
-2
-3
LOG10(CONC)
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17
SAMPLING STATION NUMBER


NICKEL, unfilt. tot. mg/l as Ni
PWQO= 0.025000
LOG10(CONC)
LOG10(PWQO)
0
-1
-2
-3
-4
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17
SAMPLING STATION NUMBER


STRONTIUM, unfilt. tot. mg/l as Sr
LOG10(CONC)
1
0
-1
-2
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17
SAMPLING STATION NUMBER



VANADIUM, unfilt. tot. mg/l as V
LOG10(CONC)
-1
-2
-3
-4
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17
SAMPLING STATION NUMBER



ZINC, unfilt. tot. mg/l as Zn
PWQO= 0.030000
LOG10(CONC)
LOG10(PWQO)
0
-1
-2
-3
-4
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17
SAMPLING STATION NUMBER

APPENDIX C

RESULTS OF MONTE CARLO SIMULATION

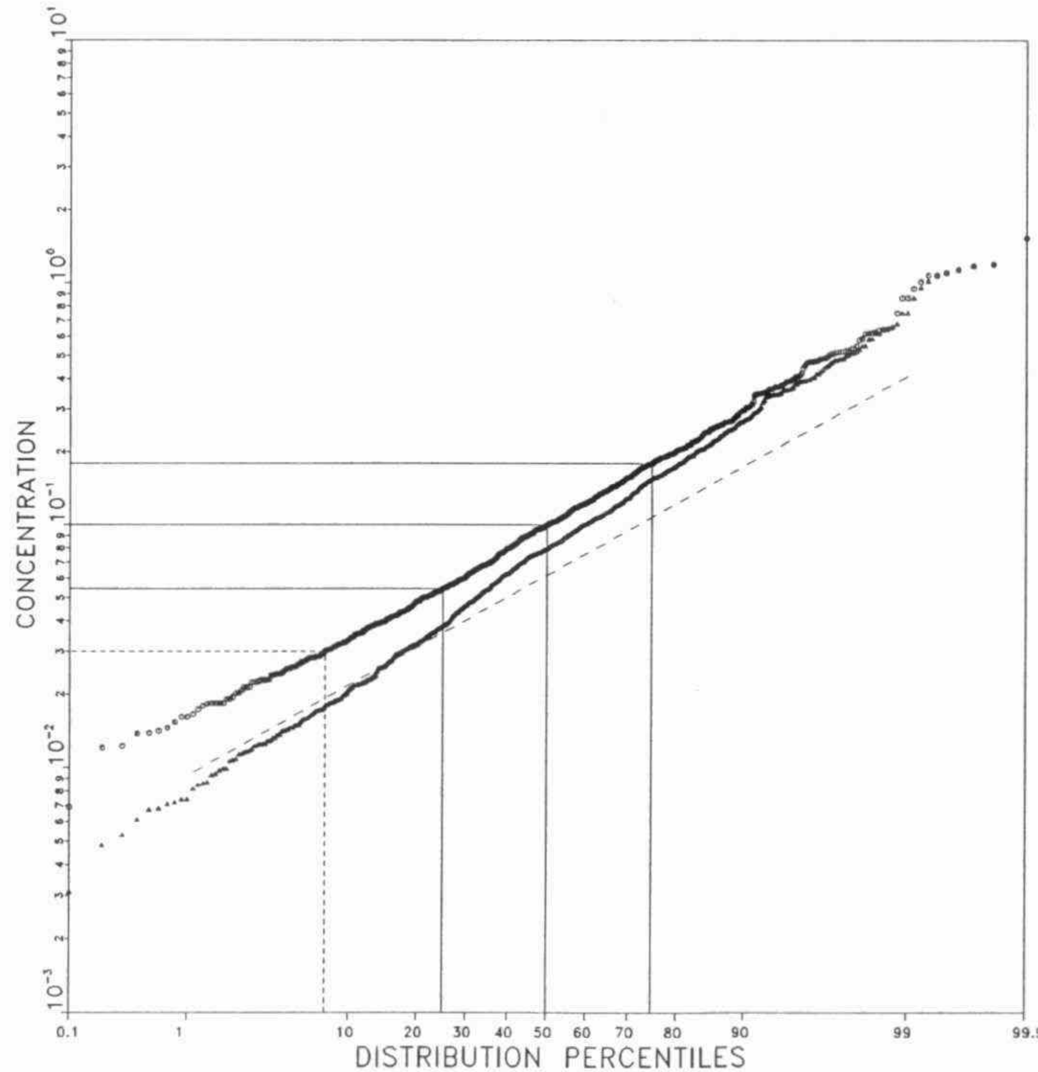
SIMULATION RESULTS FOR

PHOSPHORUS FOR VARYING

EFFLUENT QUALITY AND

DESIGN FLOW

PHOSPHORUS REDUCTION - MEAN CONC. = 1.0251 mg/l



LEGEND

OBSERVED DATA

upstream concentrations - △

downstream concentrations - - - - - -

upstream excursions 82.3 %

PREDICTIONS

downstream concentrations - ○

75th percentile =0.17920 mg/l

50th percentile =0.09970 mg/l

25th percentile =0.05460 mg/l

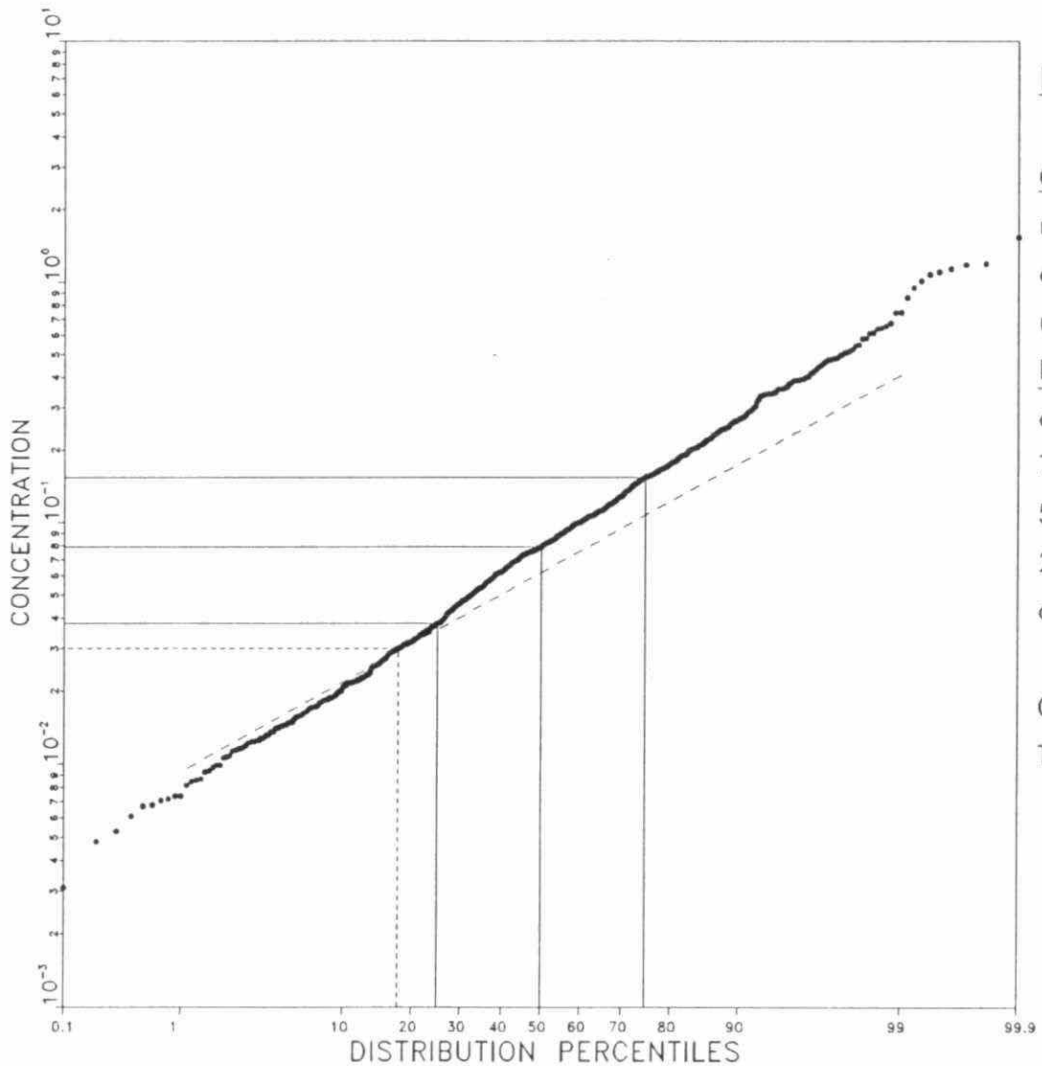
downstream excursions 92.4 %

Criteria= 0.03000 mg/l

Type of Criteria :PWQG

Eff. flow = 0.526 m^3/s

PHOSPHORUS REDUCTION – EFF. CONC. = BACKGROUND



LEGEND

OBSERVED DATA

upstream concentrations – △

downstream concentrations - - - - - -

upstream excursions 82.3 %

PREDICTIONS

downstream concentrations – ○

75th percentile =0.15410 mg/l

50th percentile =0.07920 mg/l

25th percentile =0.03820 mg/l

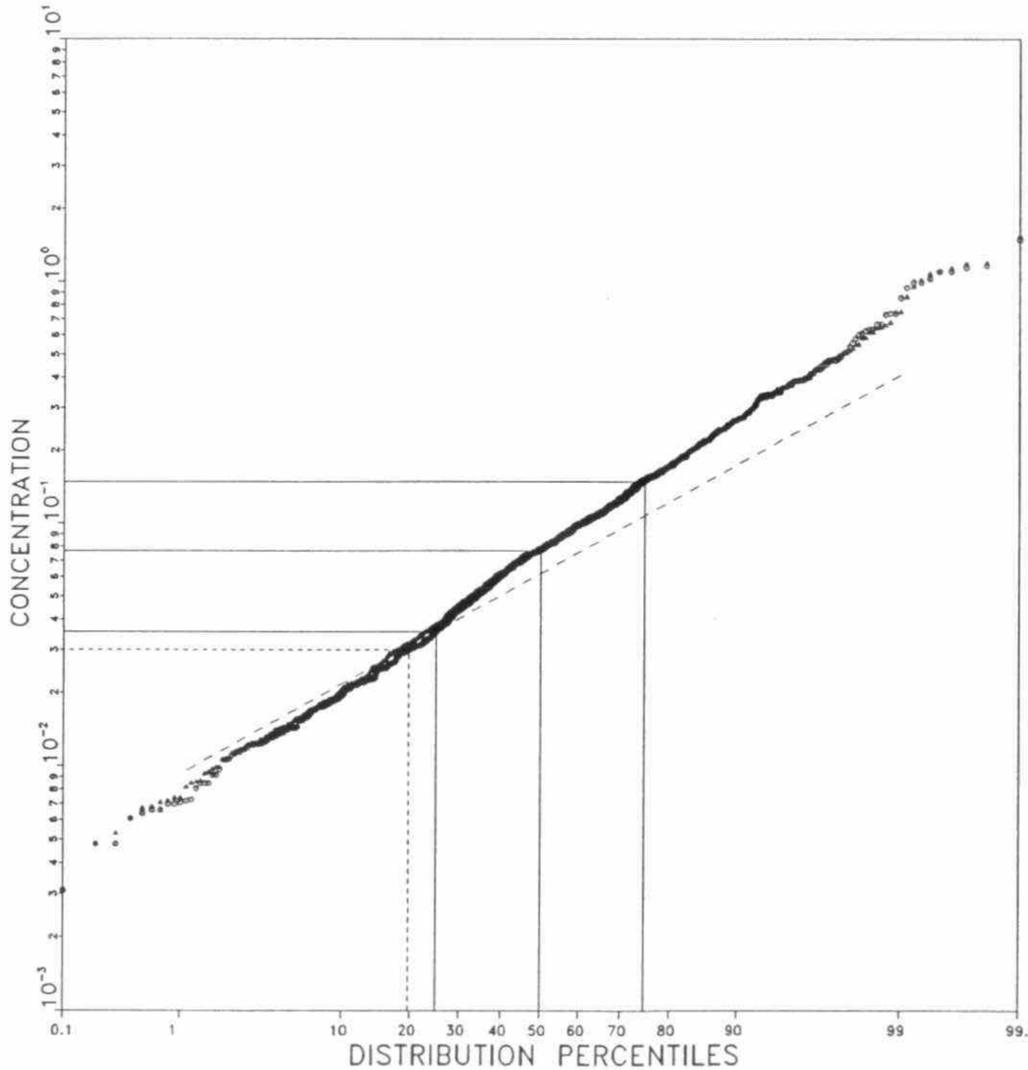
downstream excursions 82.3 %

Criteria= 0.03000 mg/l

Type of Criteria :PWQG

Eff. flow = 0.526 m^3/s

PHOSPHORUS REDUCTION – EFF. CONC. = 0.0



LEGEND

OBSERVED DATA

upstream concentrations –

downstream concentrations

upstream excursions 82.3 %

PREDICTIONS

downstream concentrations –

75th percentile =0.14800 mg/l

50th percentile =0.07700 mg/l

25th percentile =0.03570 mg/l

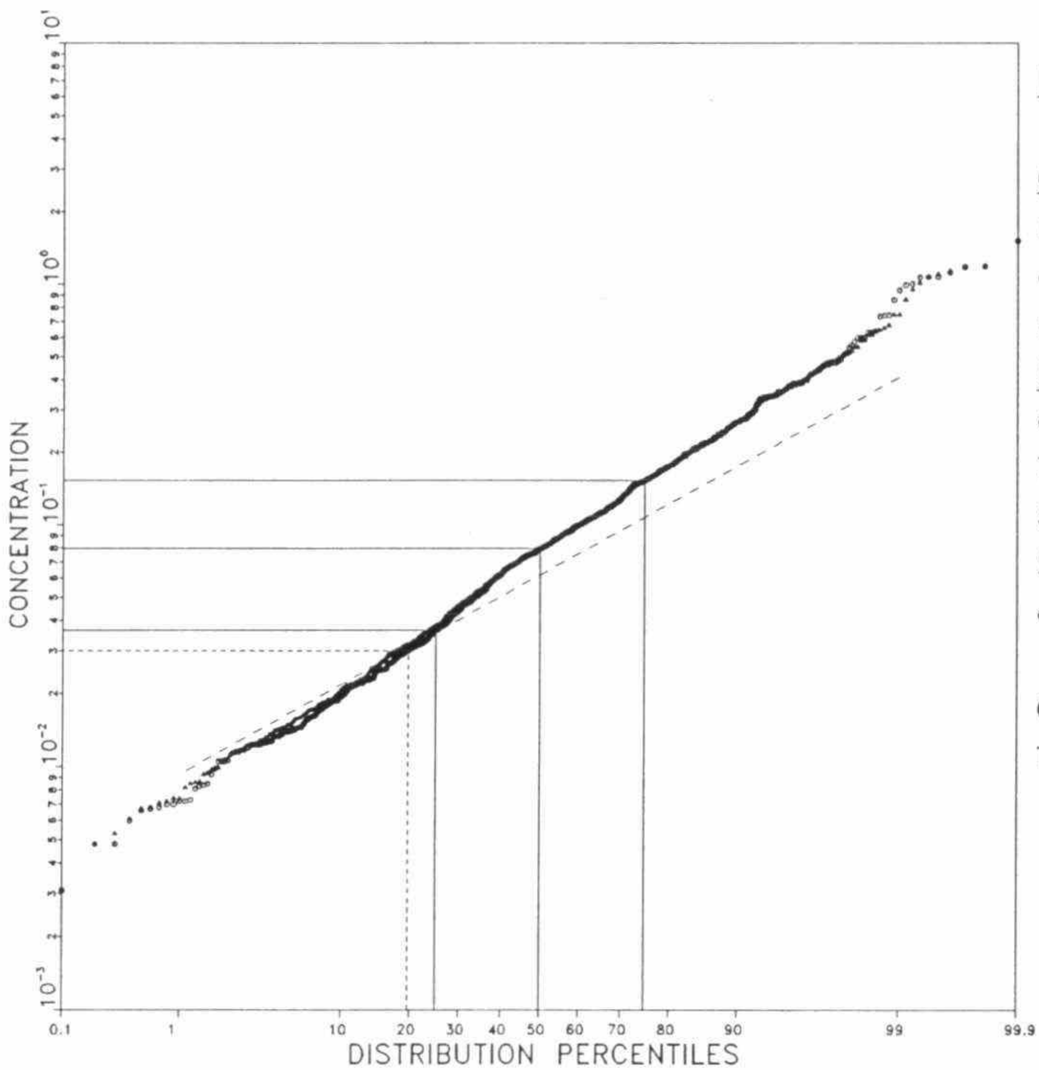
downstream excursions 80.4 %

Criteria= 0.03000 mg/l

Type of Criteria :PWQG

Eff. flow = 0.526 m^3/s

PHOSPHORUS REDUCTION 20% MED. 50% VAR.



LEGEND

OBSERVED DATA

upstream concentrations – △

downstream concentrations - - - - - -

upstream excursions 82.3 %

PREDICTIONS

downstream concentrations – ○

75th percentile =0.15250 mg/l

50th percentile =0.07950 mg/l

25th percentile =0.03650 mg/l

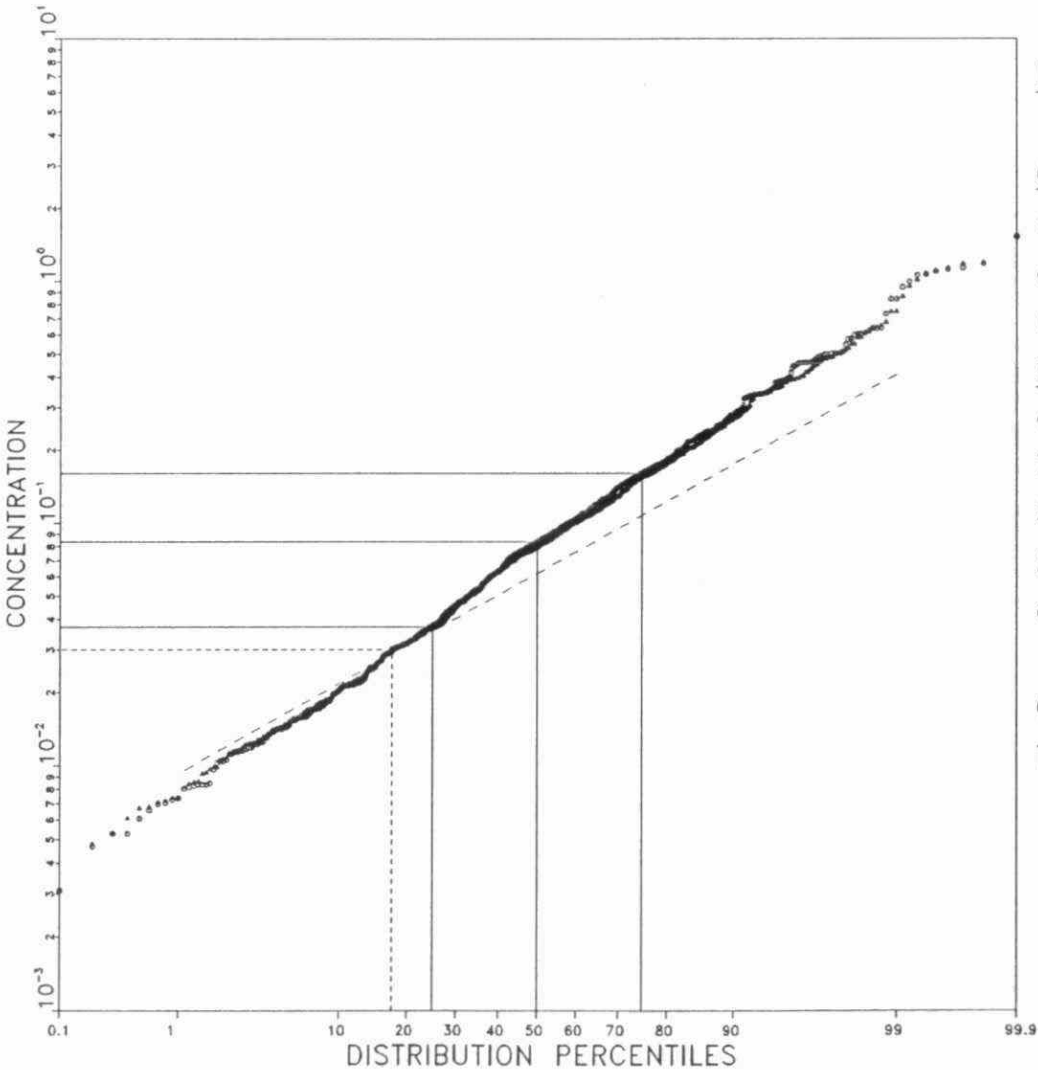
downstream excursions 80.3 %

Criteria= 0.03000 mg/l

Type of Criteria :PWQG

Eff. flow = 0.526 m^3/s

PHOSPHORUS REDUCTION 0% MED. 75% VAR.



LEGEND

OBSERVED DATA

upstream concentrations – △

downstream concentrations - - - - - -

upstream excursions 82.3 %

PREDICTIONS

downstream concentrations – o

75th percentile =0.16050 mg/l

50th percentile =0.08370 mg/l

25th percentile =0.03730 mg/l

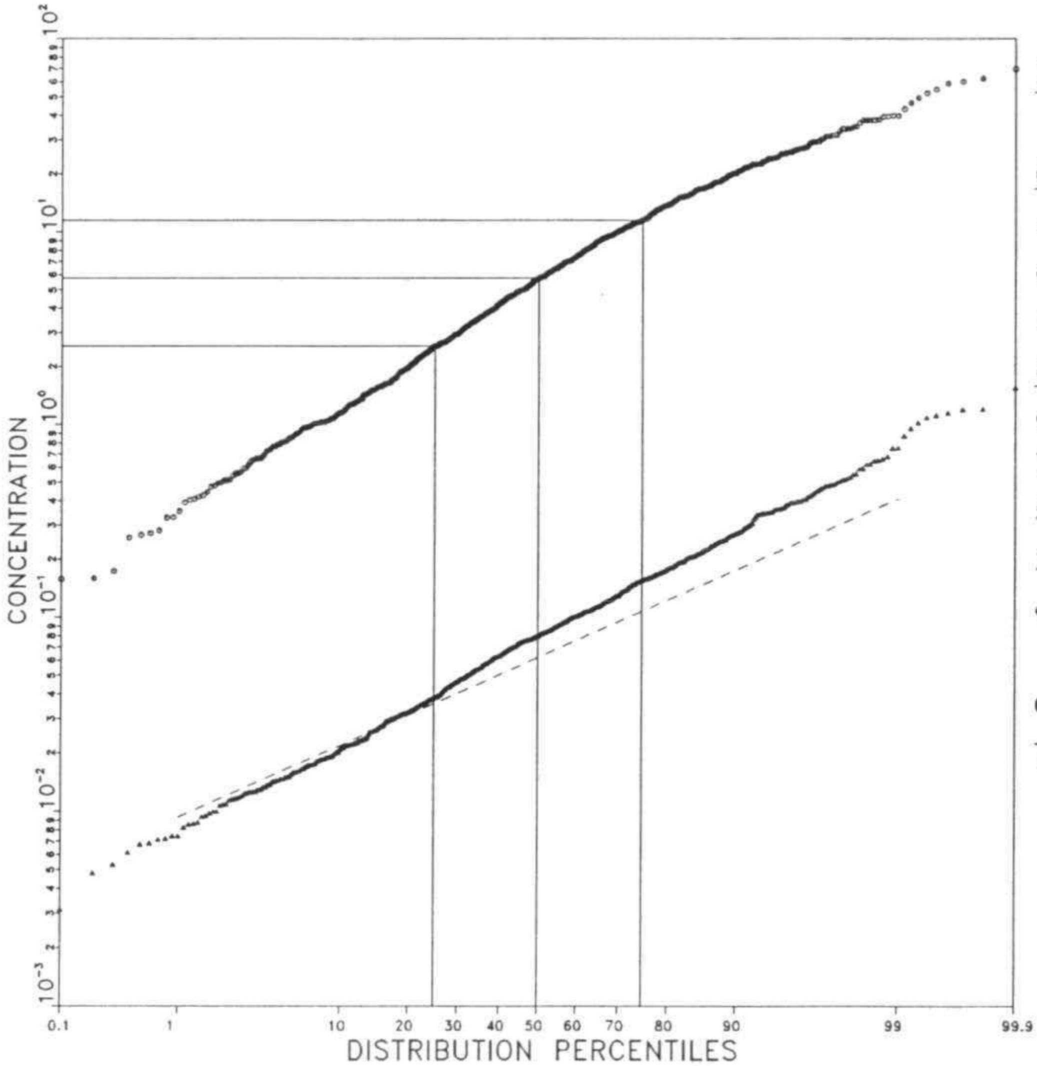
downstream excursions 82.7 %

Criteria= 0.03000 mg/l

Type of Criteria :PWQG

Eff. flow = 0.526 m^3/s

PHOSPHORUS REDUCTION 20% MED. 50% VAR.



LEGEND

OBSERVED DATA

upstream concentrations – △

downstream concentrations - - - - - -

upstream excursions 82.3 %

PREDICTIONS

downstream concentrations – ○

75th percentile =11.46230 mg/l

50th percentile =5.74170 mg/l

25th percentile =2.54860 mg/l

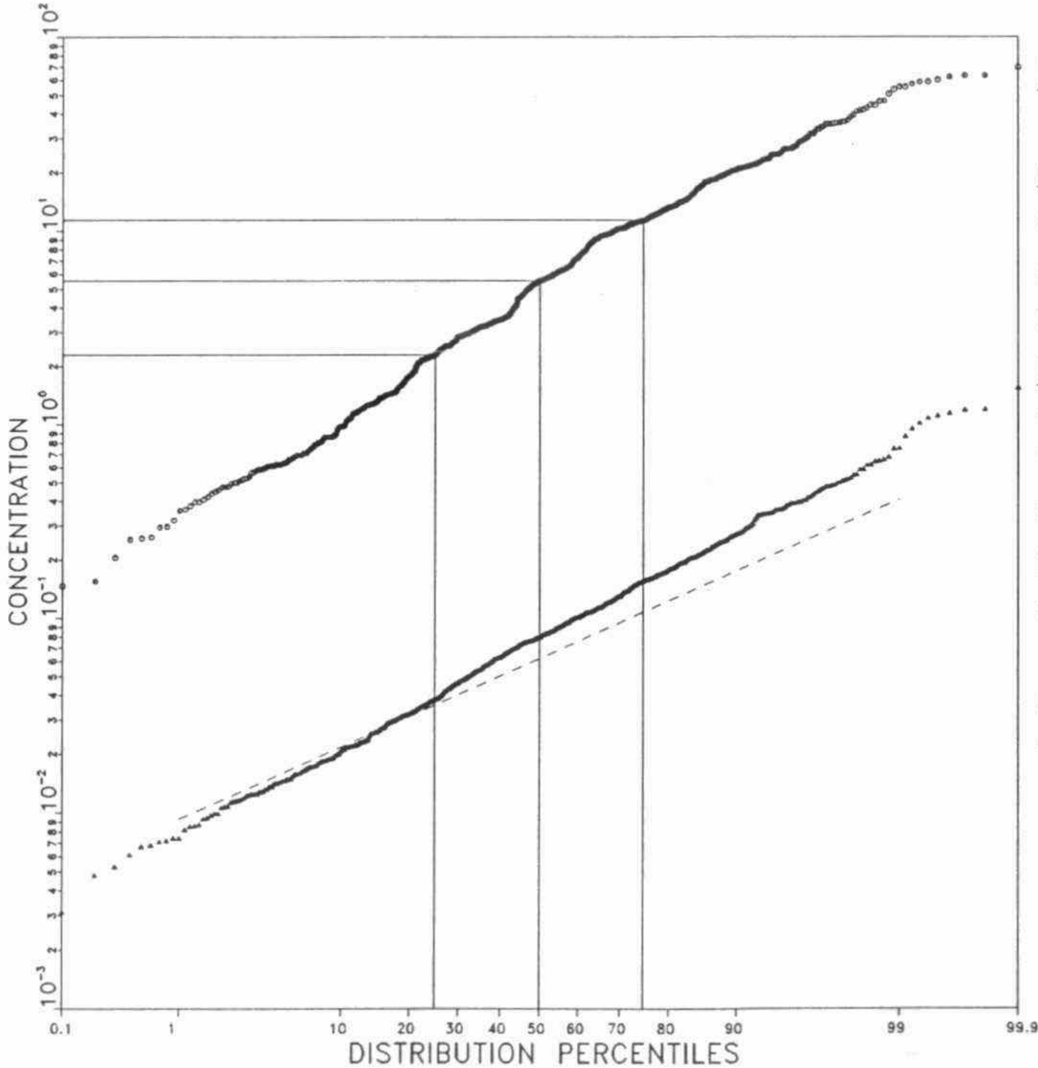
downstream excursions > 99.9 %

Criteria= 0.03000 mg/l

Type of Criteria :PWQG

Eff. flow = 0.841 m^3/s

PHOSPHORUS REDUCTION 0% MED. 75% VAR.



LEGEND

OBSERVED DATA

upstream concentrations –

downstream concentrations

upstream excursions 82.3 %

PREDICTIONS

downstream concentrations –

75th percentile =11.35170 mg/l

50th percentile =5.53580 mg/l

25th percentile =2.29220 mg/l

downstream excursions > 99.9 %

Criteria= 0.03000 mg/l

Type of Criteria :PWQG

Eff. flow = 0.841 m^3/s

SIMULATION RESULTS

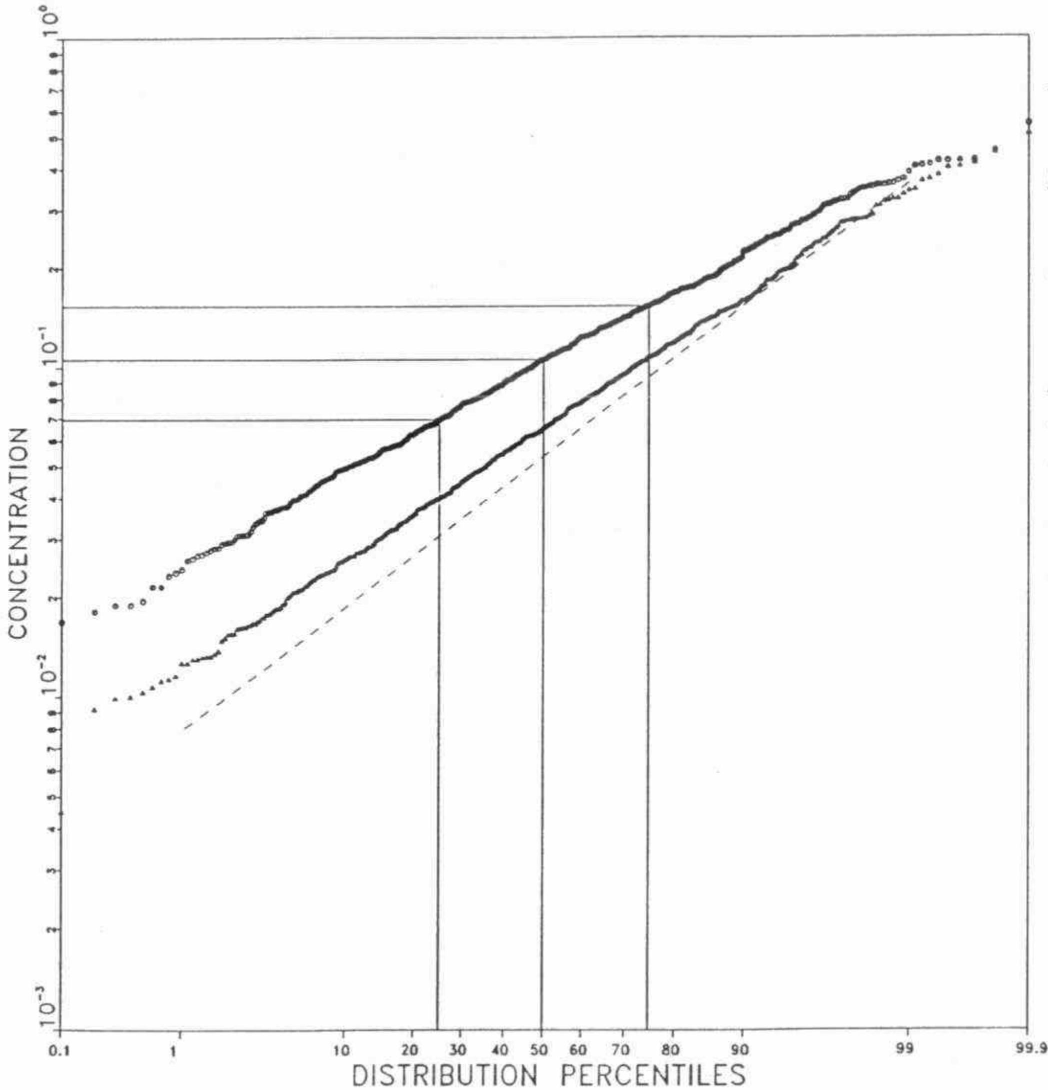
BY PARAMETER

WITH EFFLUENT CHARACTERISTICS

FOR DESIGN CAPACITY

= 0.526 M^3/S

MONTE CARLO SIMULATION – TOTAL AMMONIA



LEGEND

OBSERVED DATA

upstream concentrations – △

downstream concentrations - - - - - -

PREDICTIONS

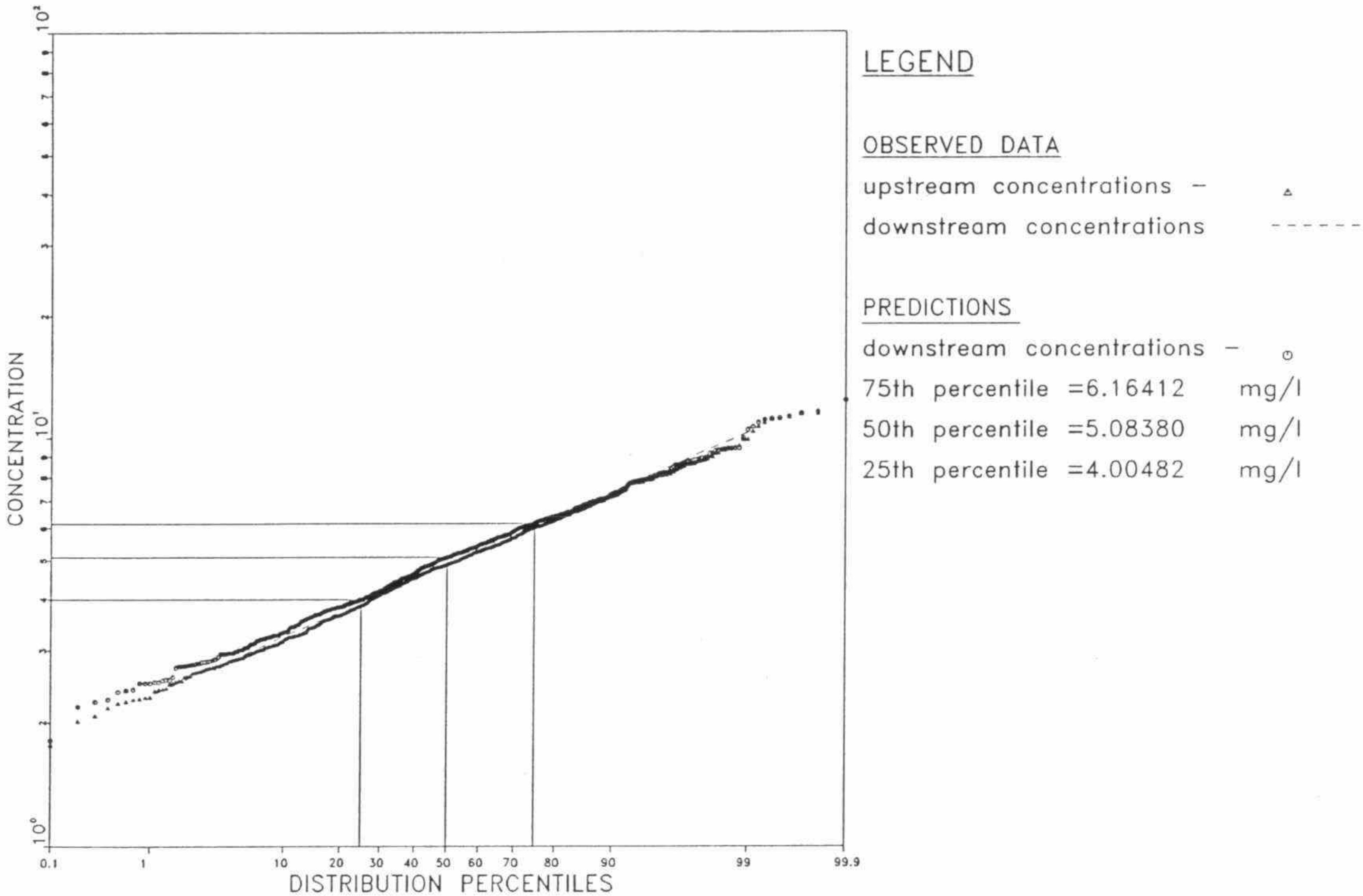
downstream concentrations – ○

75th percentile =0.15344 mg/l

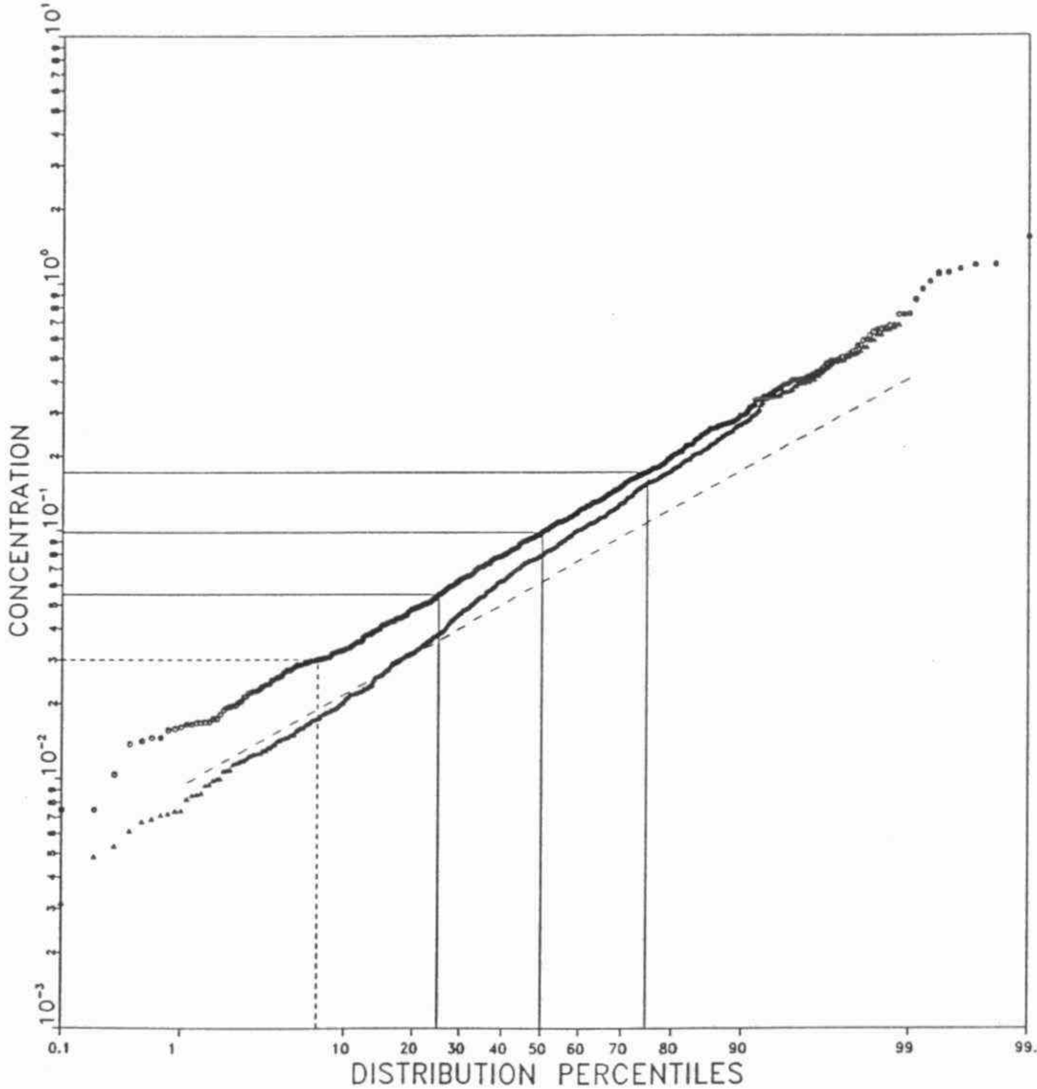
50th percentile =0.10562 mg/l

25th percentile =0.06942 mg/l

MONTE CARLO SIMULATION – ORGANIC CARBON



MONTE CARLO SIMULATION – PHOSPHORUS



LEGEND

OBSERVED DATA

upstream concentrations – △

downstream concentrations - - - - - -

upstream excursions 82.3 %

PREDICTIONS

downstream concentrations – o

75th percentile =0.17120 mg/l

50th percentile =0.09827 mg/l

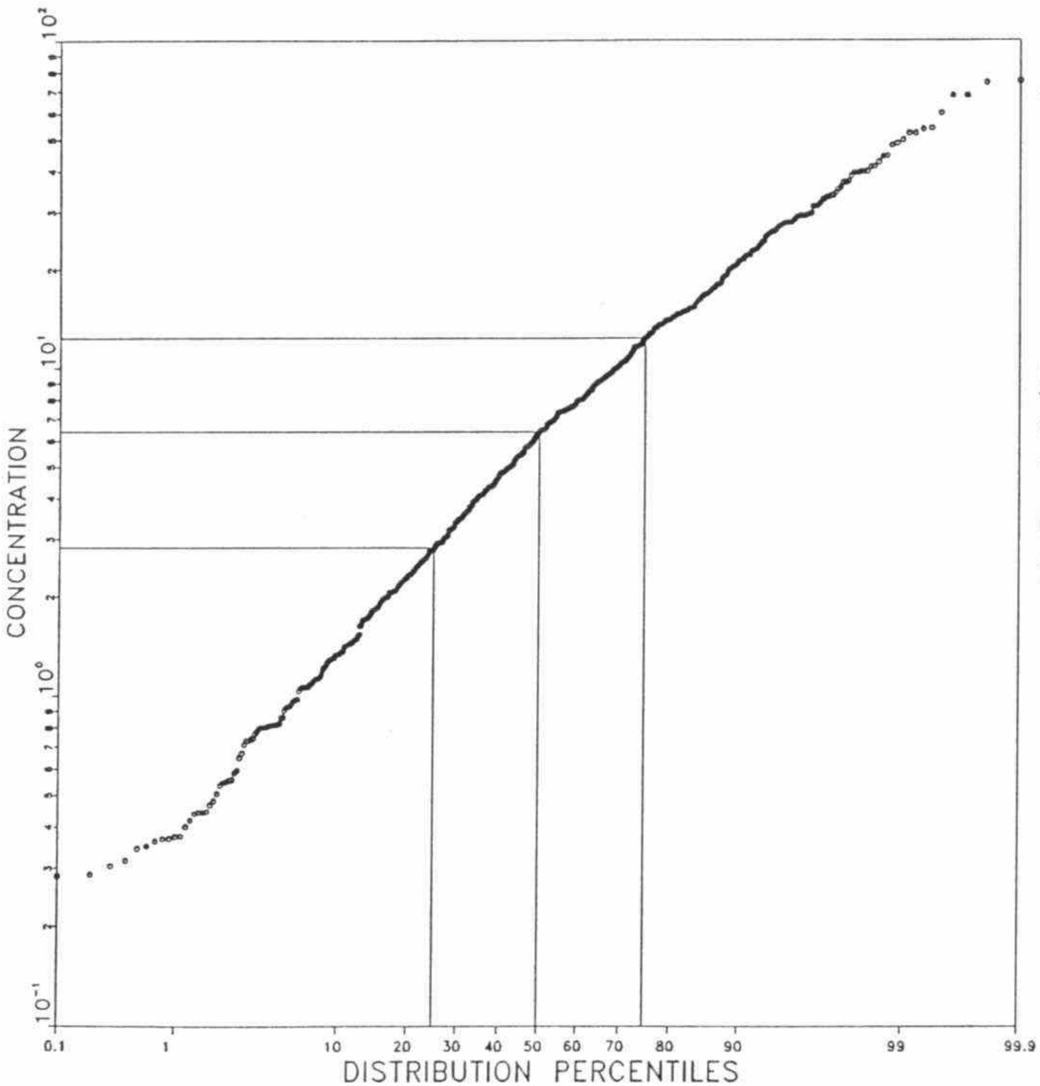
25th percentile =0.05527 mg/l

downstream excursions 92.7 %

Criteria= 0.03000 mg/l

Type of Criteria : PWQG

MONTE CARLO SIMULATION - FILTERED P



LEGEND

PREDICTIONS

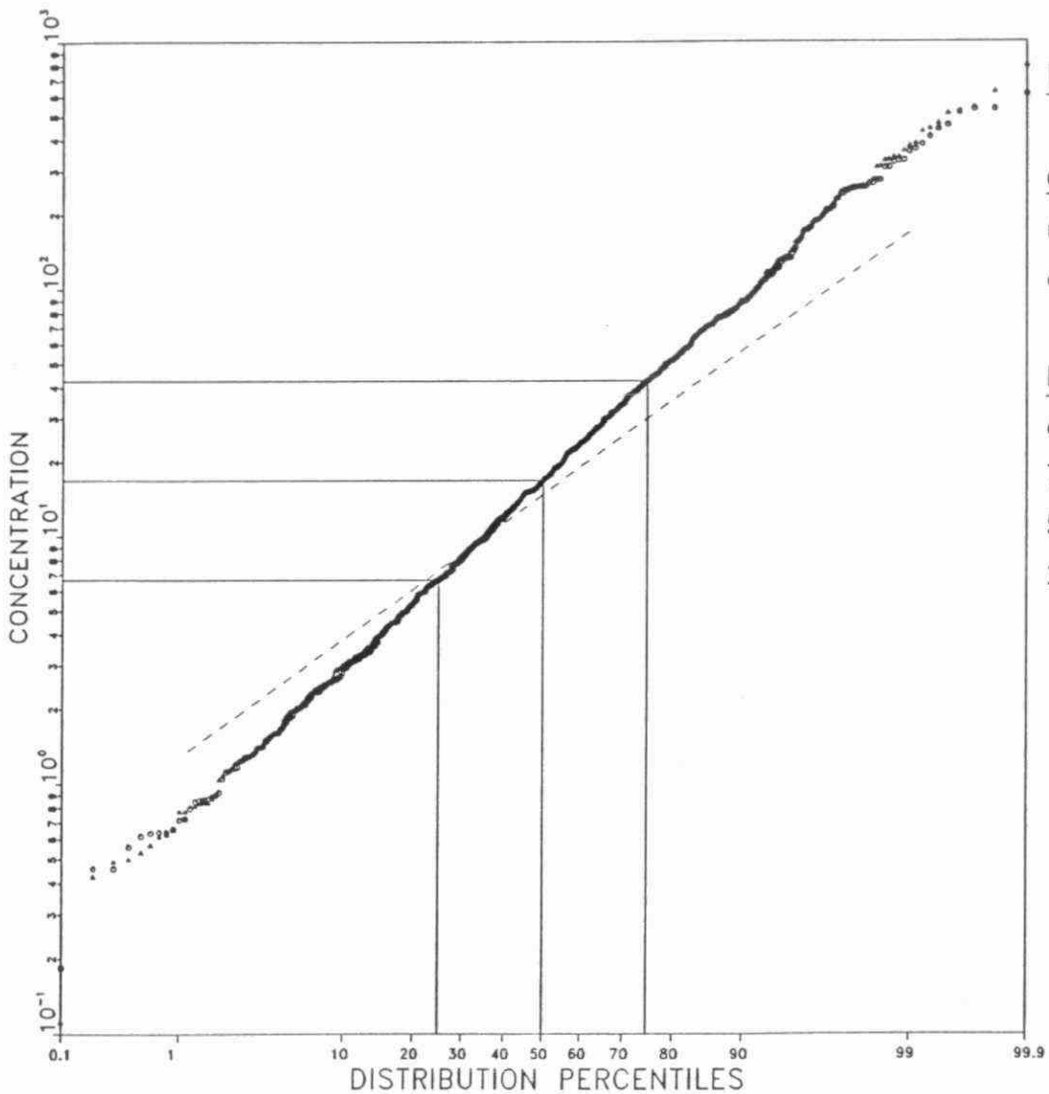
downstream concentrations - ⊙

75th percentile =12.37813 mg/l

50th percentile =6.40315 mg/l

25th percentile =2.82493 mg/l

MONTE CARLO SIMULATION – SUSPENDED SOLIDS



LEGEND

OBSERVED DATA

upstream concentrations – △

downstream concentrations - - - - - -

PREDICTIONS

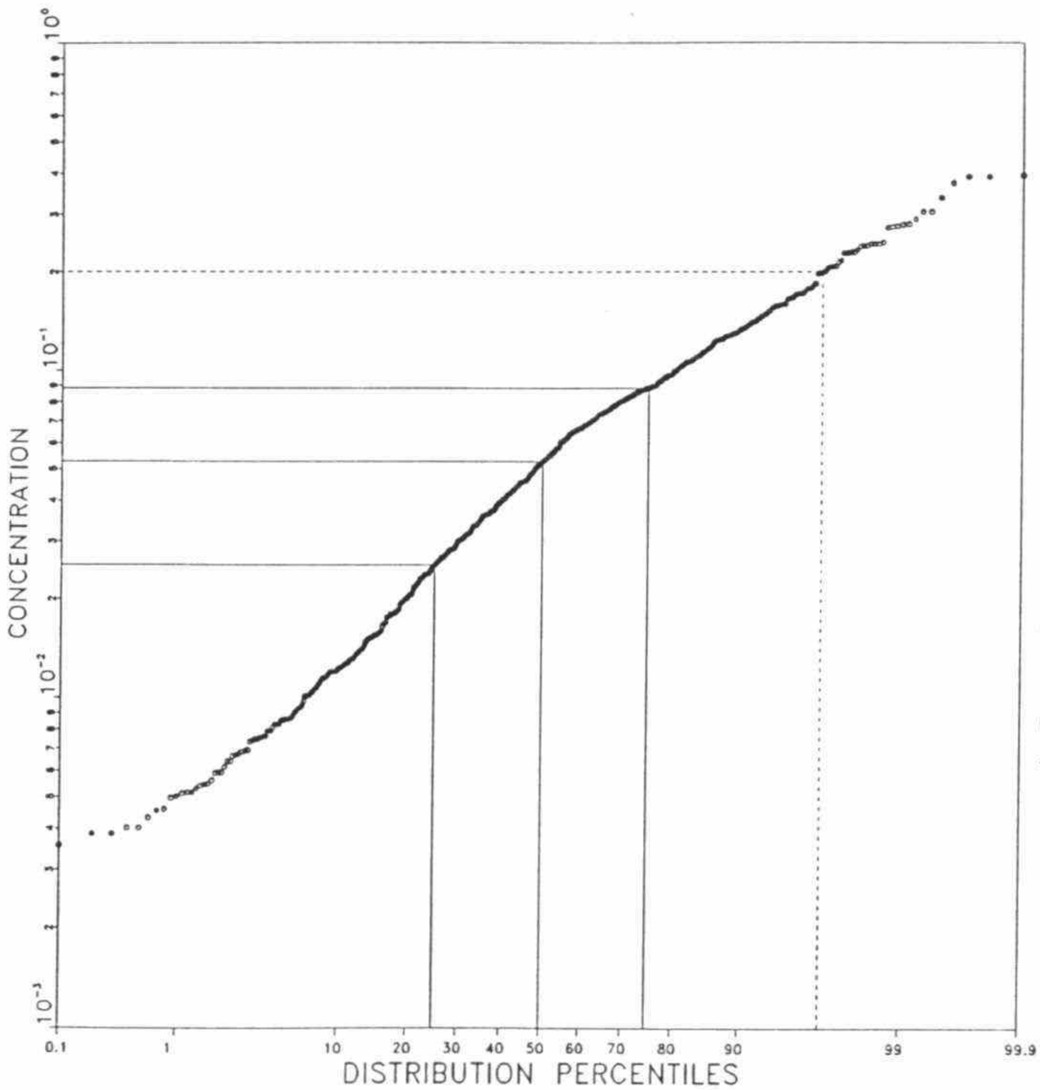
downstream concentrations – o

75th percentile =42.51508 mg/l

50th percentile =16.80600 mg/l

25th percentile =6.65422 mg/l

MONTE CARLO SIMULATION - CADMIUM



LEGEND

PREDICTIONS

downstream concentrations - o

75th percentile =0.08828 ug/l

50th percentile =0.05277 ug/l

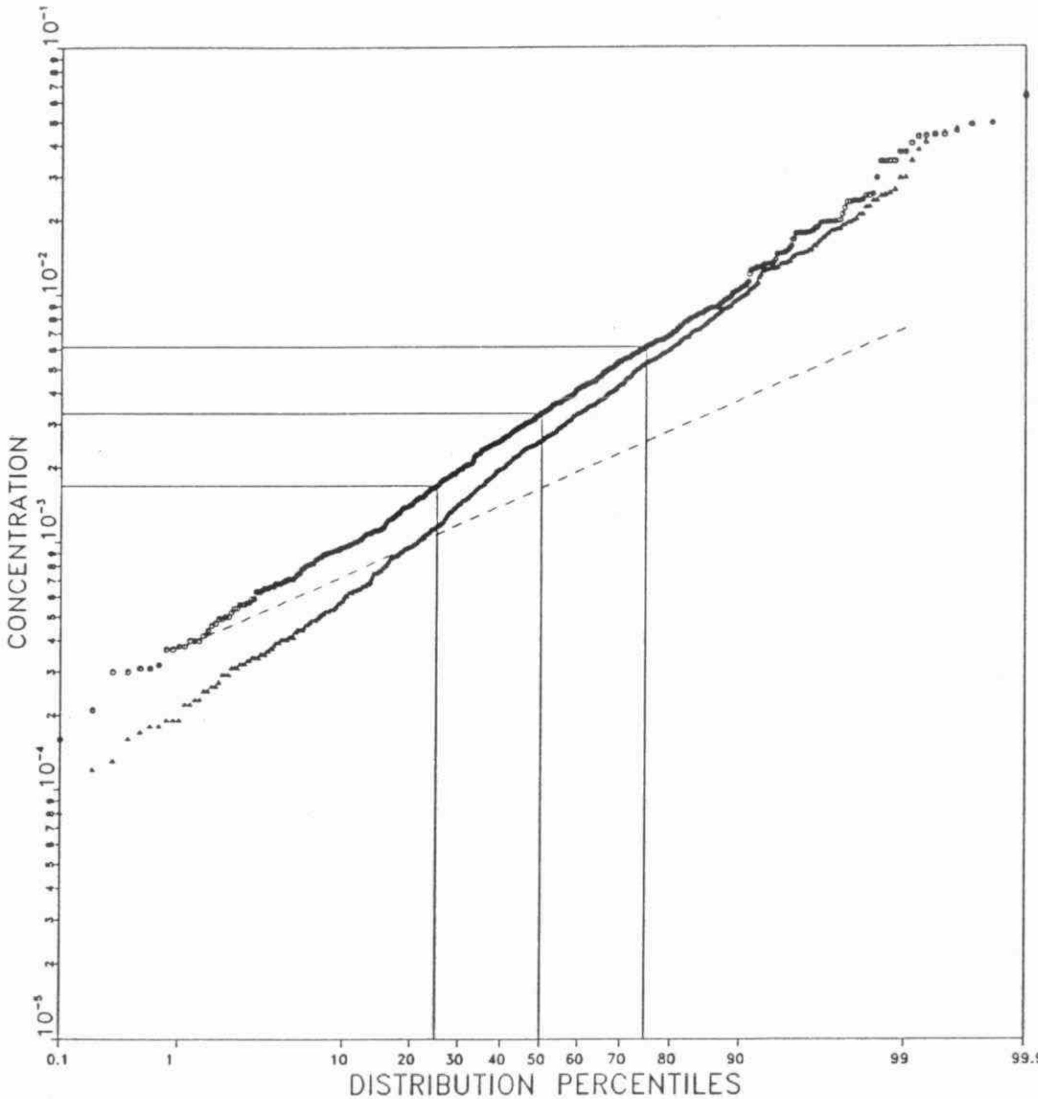
25th percentile =0.02544 ug/l

downstream excursions 3.5 %

Criteria= 0.2 ug/l

Type of Criteria : PWQO

MONTE CARLO SIMULATION – CHROMIUM



LEGEND

OBSERVED DATA

upstream concentrations – ▵

downstream concentrations - - - - - -

upstream excursions < 0.1 %

PREDICTIONS

downstream concentrations – o

75th percentile =0.00615 mg/l

50th percentile =0.00331 mg/l

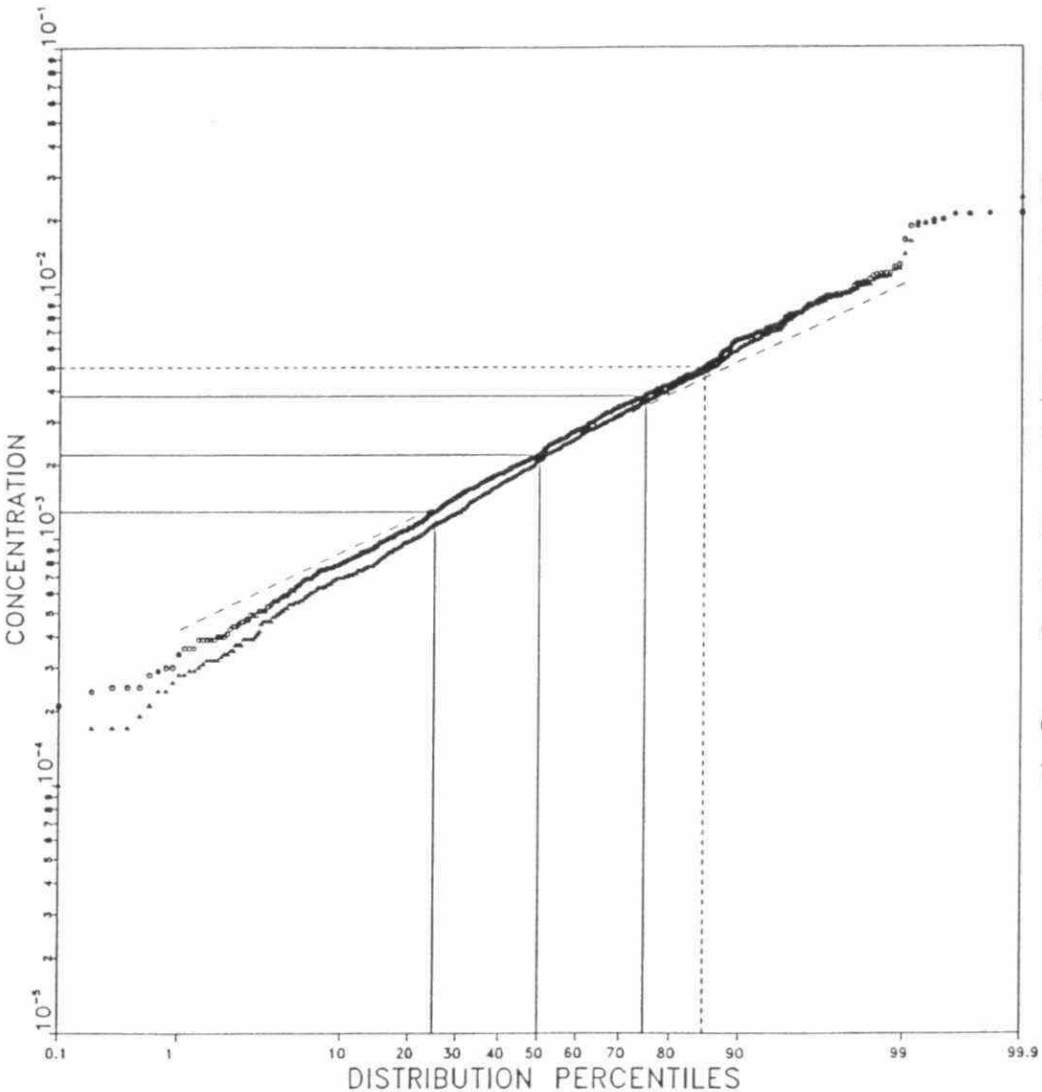
25th percentile =0.00169 mg/l

downstream excursions < 0.1 %

Criteria= 0.10000 mg/l

Type of Criteria : PWQO

MONTE CARLO SIMULATION – COPPER



LEGEND

OBSERVED DATA

upstream concentrations – △

downstream concentrations - - - - - -

upstream excursions 13.1 %

PREDICTIONS

downstream concentrations – o

75th percentile =0.00382 mg/l

50th percentile =0.00220 mg/l

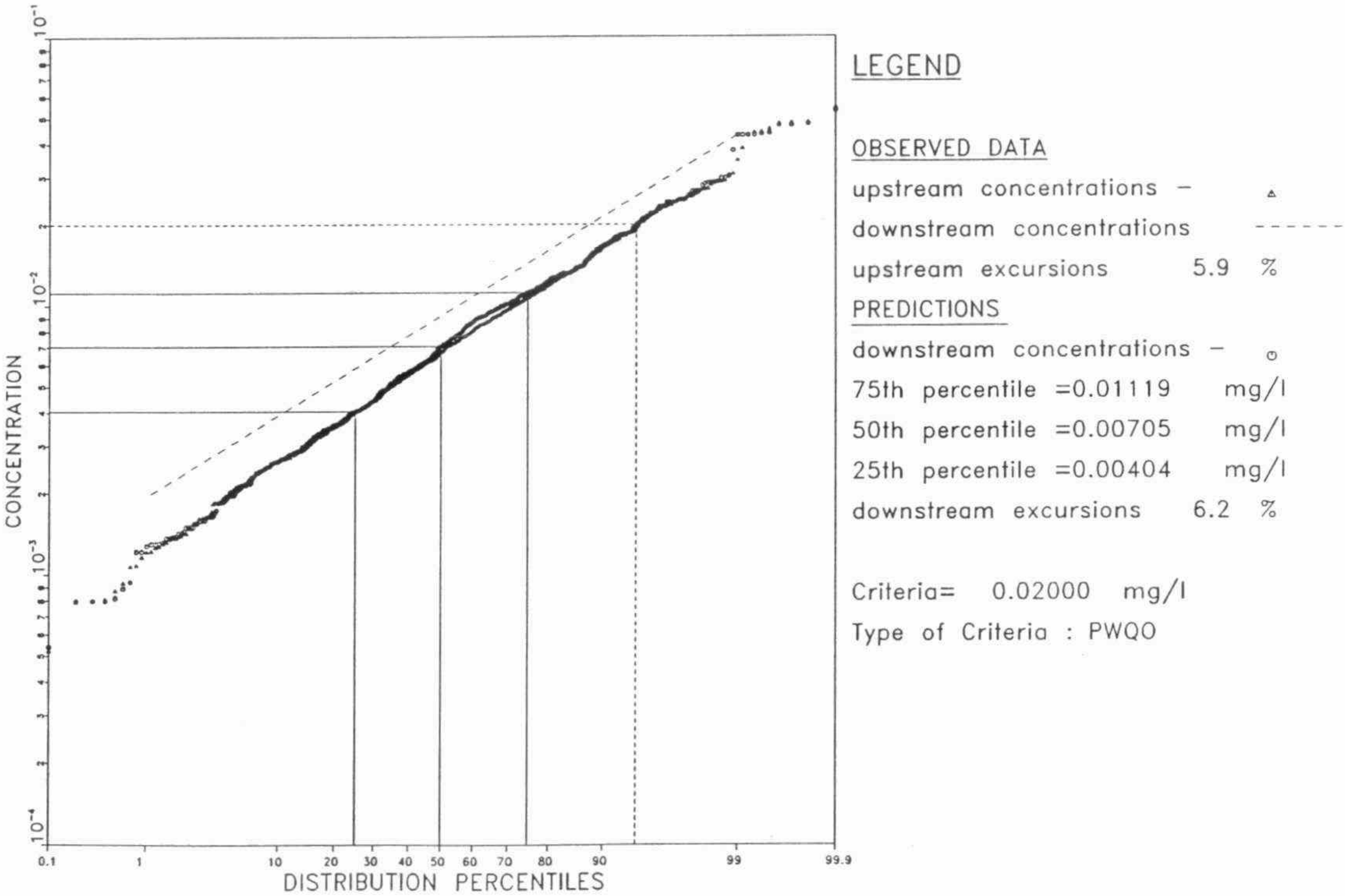
25th percentile =0.00129 mg/l

downstream excursions 14.6 %

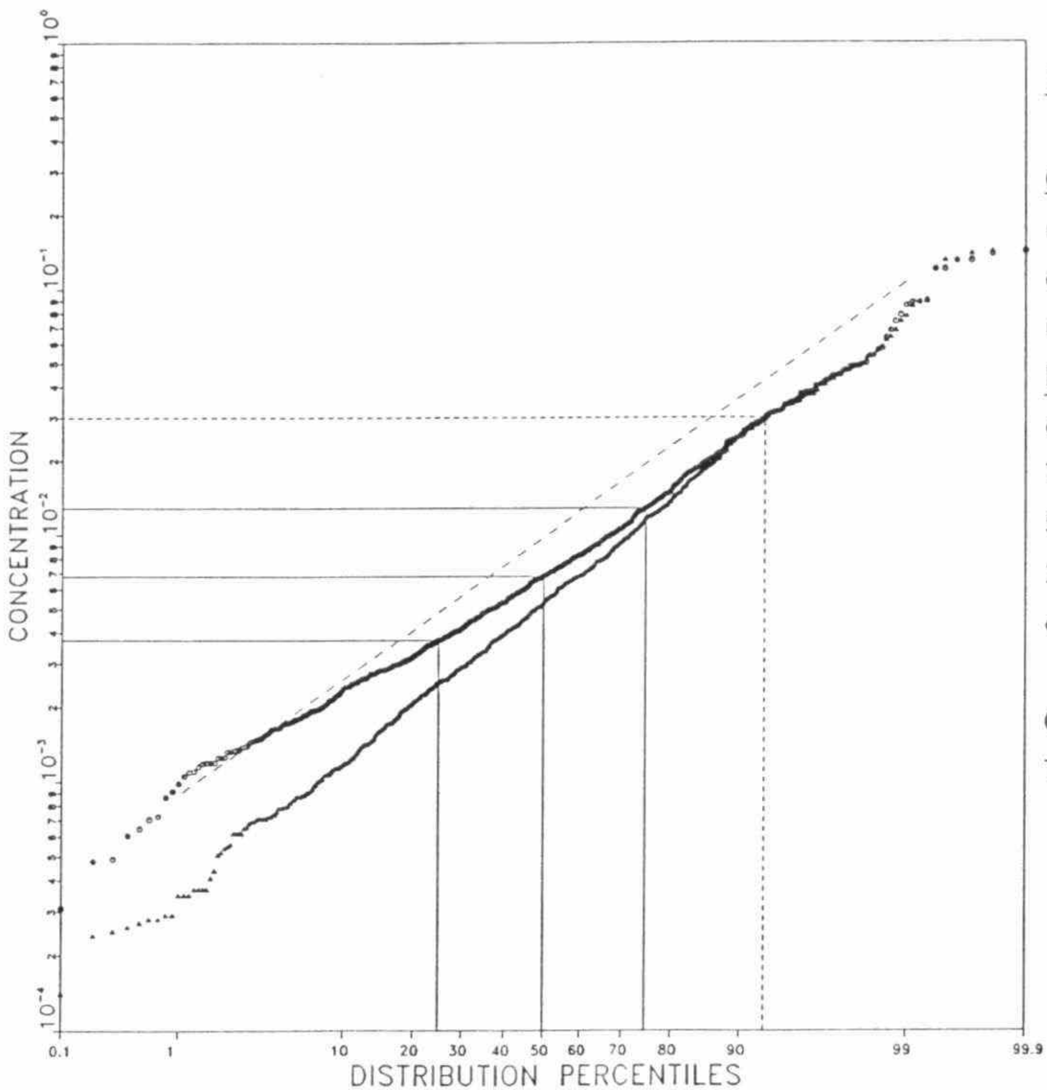
Criteria= 0.00500 mg/l

Type of Criteria : PWQO

MONTE CARLO SIMULATION – LEAD



MONTE CARLO SIMULATION – ZINC



LEGEND

OBSERVED DATA

upstream concentrations – △

downstream concentrations - - - - - -

upstream excursions 7.4 %

PREDICTIONS

downstream concentrations – ○

75th percentile =0.01283 mg/l

50th percentile =0.00681 mg/l

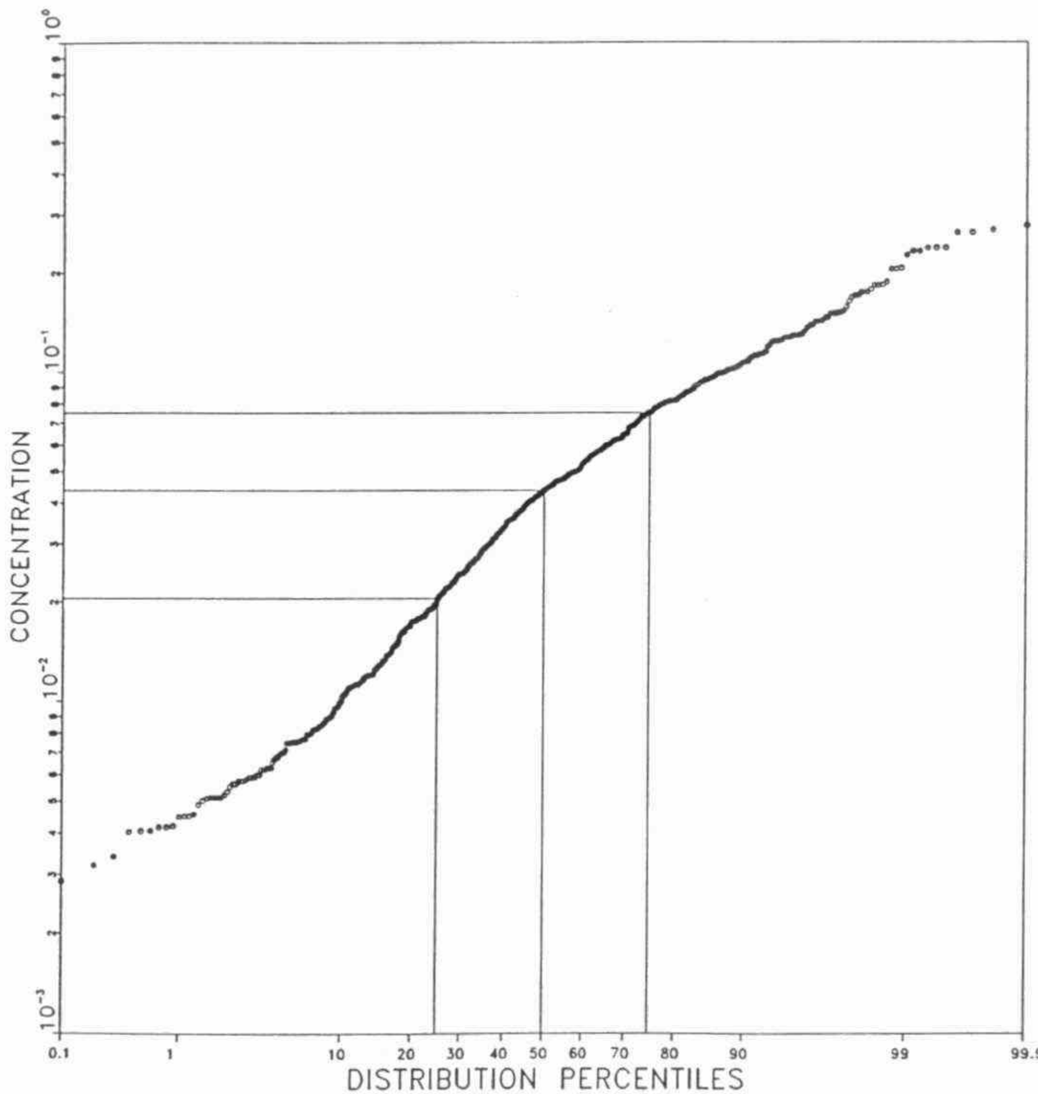
25th percentile =0.00374 mg/l

downstream excursions 7.6 %

Criteria= 0.03000 mg/l

Type of Criteria : PWQO

MONTE CARLO SIMULATION – BENZENE



LEGEND

PREDICTIONS

downstream concentrations – o

75th percentile =0.07512 ug/l

50th percentile =0.04371 ug/l

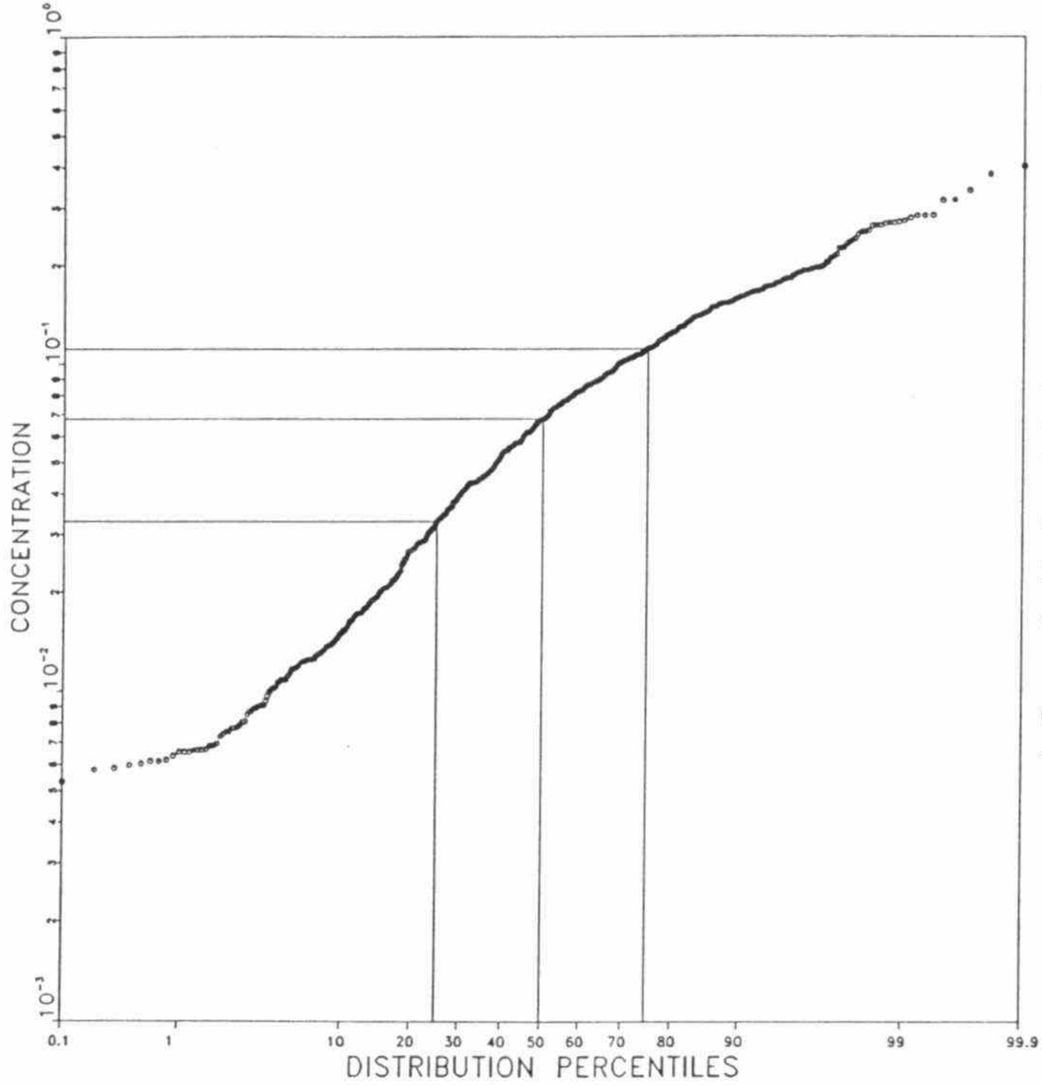
25th percentile =0.02048 ug/l

downstream excursions < 0.1 %

Criteria= 300.0 ug/l

Type of Criteria : CCREM

MONTE CARLO SIMULATION - ETHYL BENZENE



LEGEND

PREDICTIONS

downstream concentrations - o

75th percentile =0.11138 ug/l

50th percentile =0.06780 ug/l

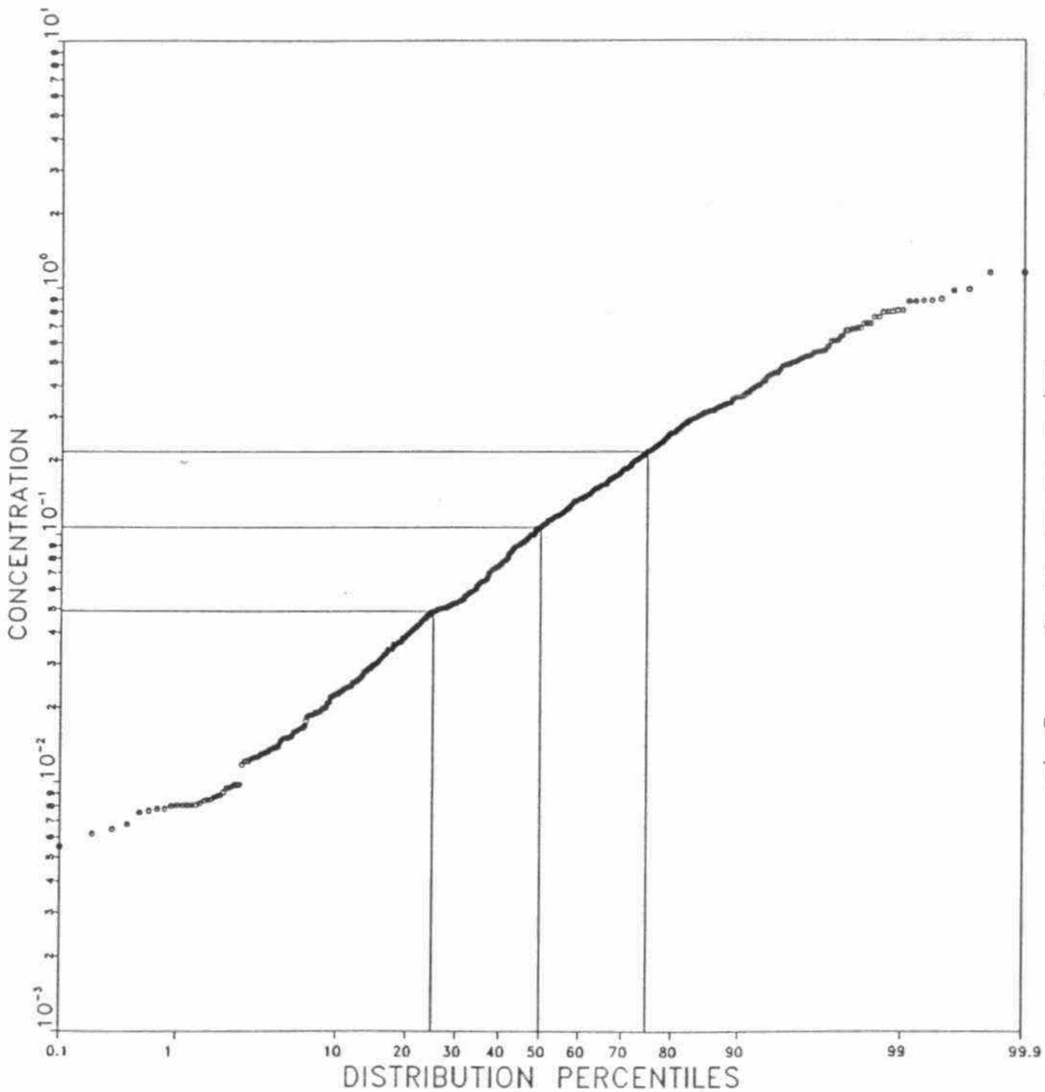
25th percentile =0.03300 ug/l

downstream excursions < 0.1 %

Criteria= 700.0 ug/l

Type of Criteria : CCREM

MONTE CARLO SIMULATION – CHLOROFORM



LEGEND

PREDICTIONS

downstream concentrations –

75th percentile =0.21663 ug/l

50th percentile =0.10707 ug/l

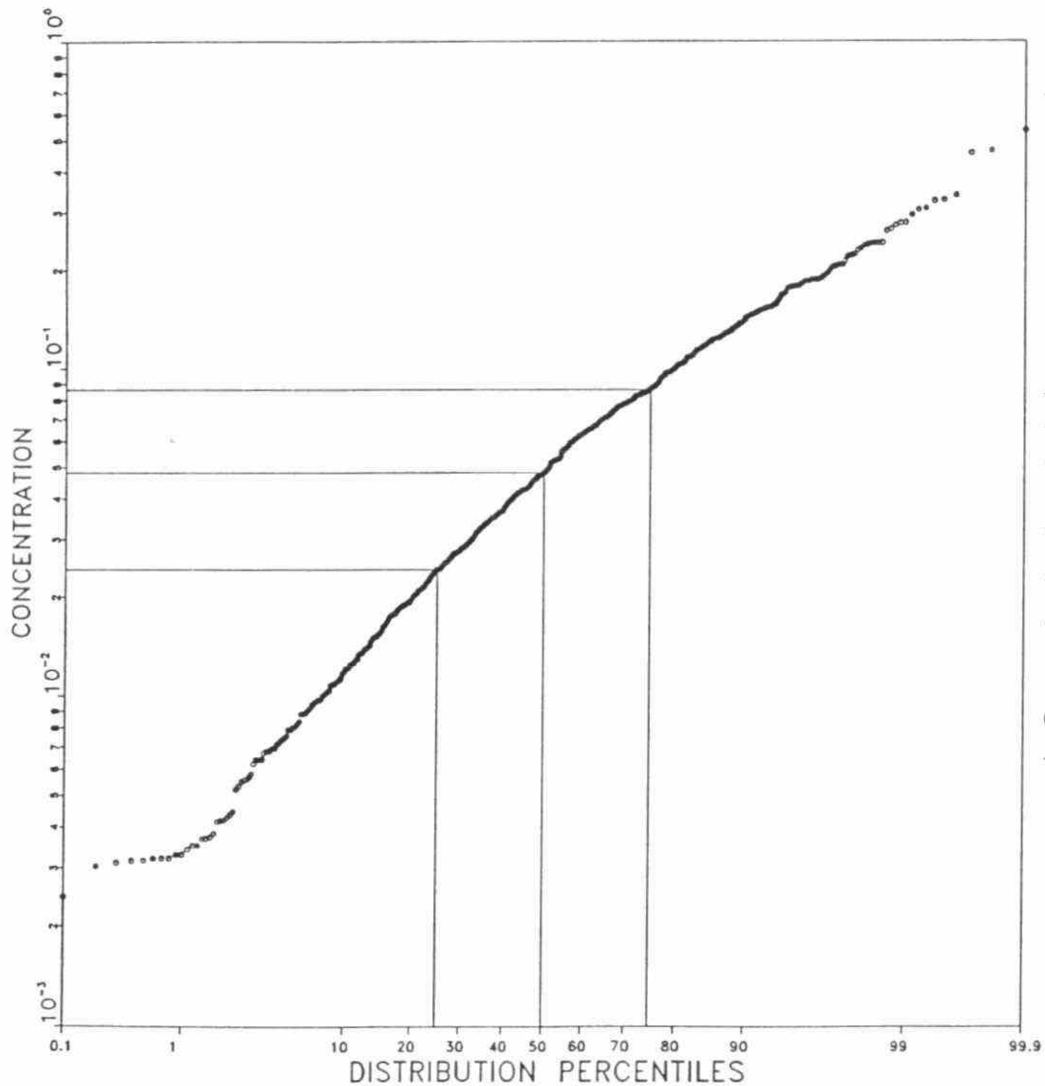
25th percentile =0.04896 ug/l

downstream excursions < 0.1 %

Criteria= 1200.0 ug/l

Type of Criteria : PWQO

MONTE CARLO SIMULATION - M- and P- XYLENES



LEGEND

PREDICTIONS

downstream concentrations - o

75th percentile =0.08636 ug/l

50th percentile =0.04800 ug/l

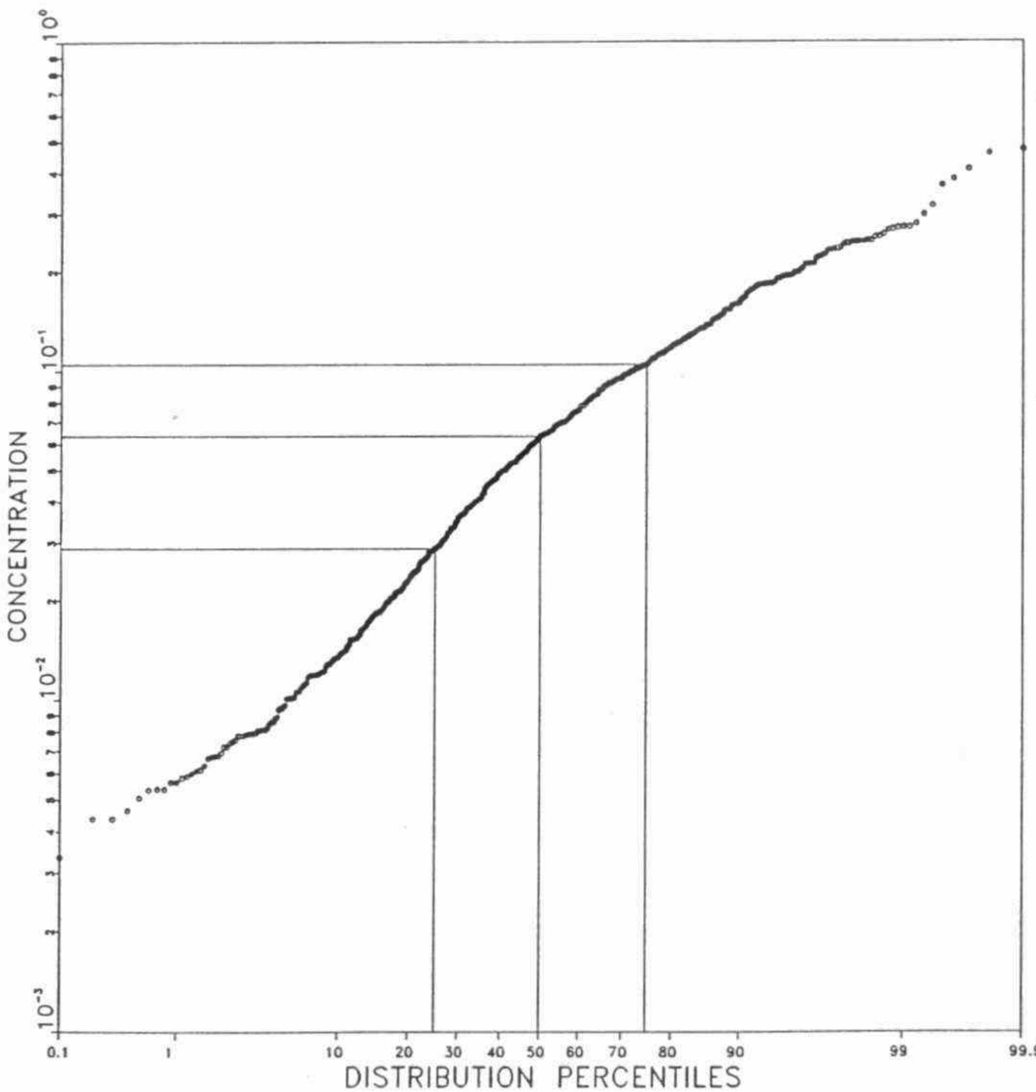
25th percentile =0.02436 ug/l

downstream excursions < 0.1 %

Criteria= 40.0 ug/l

Type of Criteria : MICHIGAN

MONTE CARLO SIMULATION - O-XYLENE



LEGEND

PREDICTIONS

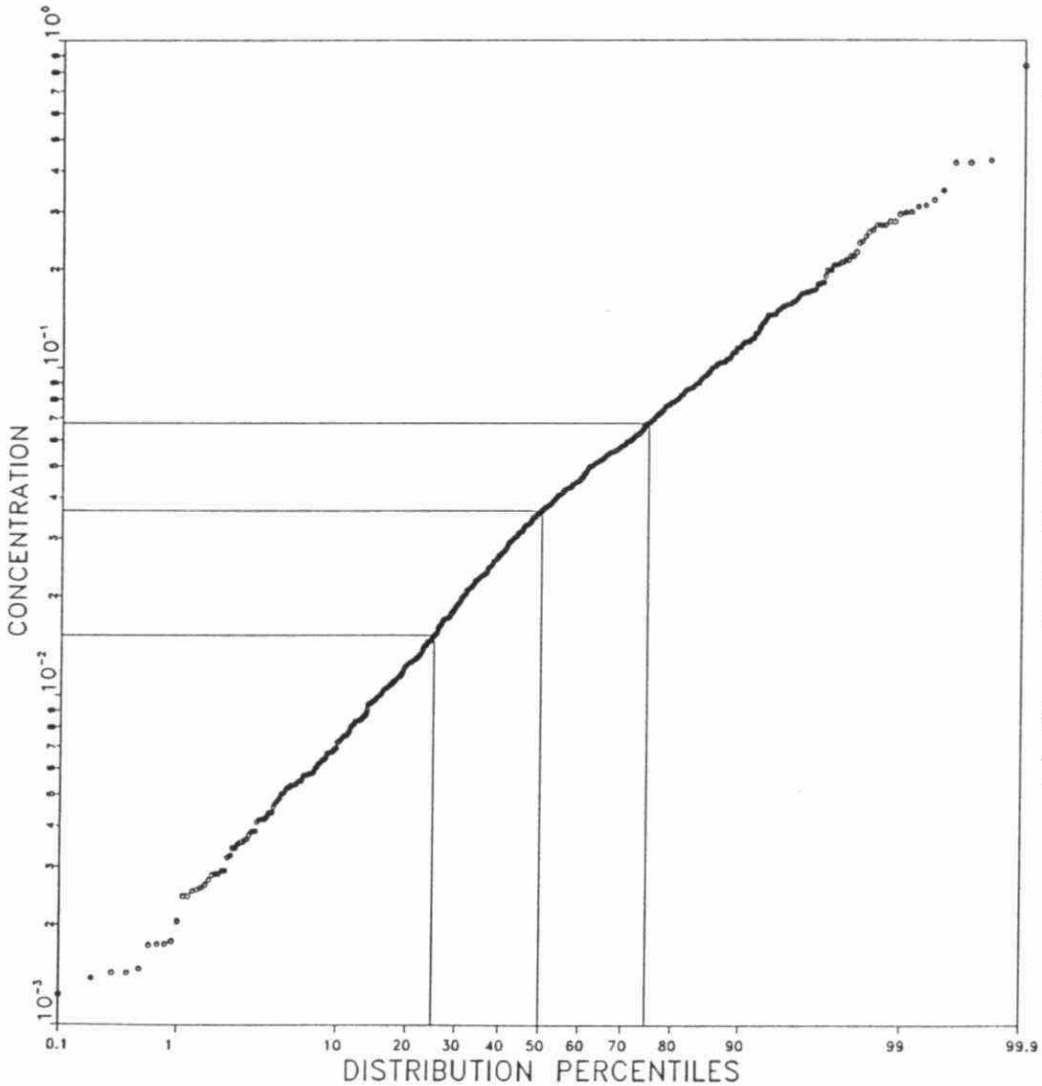
downstream concentrations - ⊙

75th percentile =0.10467 ug/l

50th percentile =0.06350 ug/l

25th percentile =0.02887 ug/l

MONTE CARLO SIMULATION – PHENOLS



LEGEND

PREDICTIONS

downstream concentrations – ○

75th percentile =0.06770 ug/l

50th percentile =0.03651 ug/l

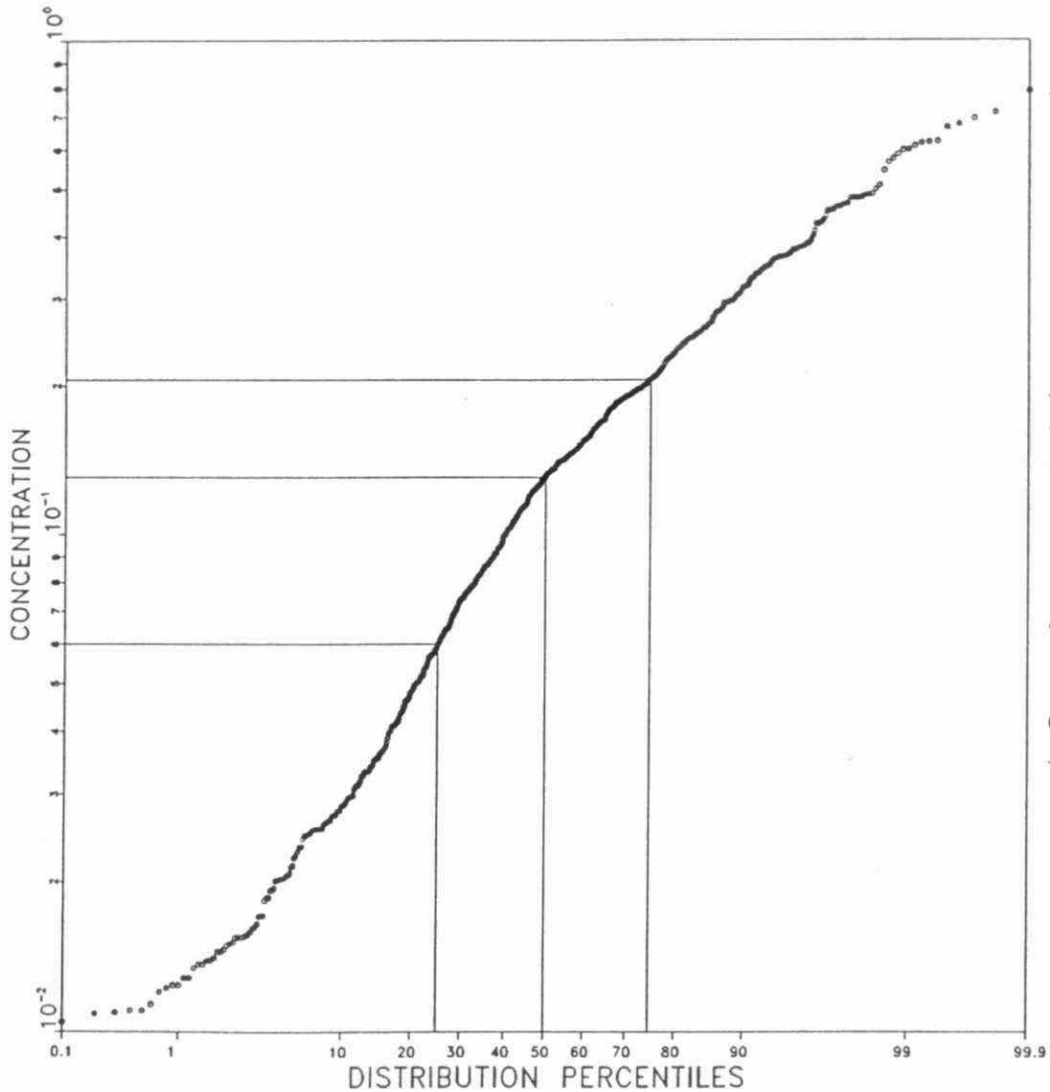
25th percentile =0.01520 ug/l

downstream excursions < 0.1 %

Criteria= 1.0 ug/l

Type of Criteria : PWQO

MONTE CARLO SIMULATION – TETRACHLOROETHYLENE



LEGEND

PREDICTIONS

downstream concentrations – ⊙

75th percentile =0.20599 ug/l

50th percentile =0.13066 ug/l

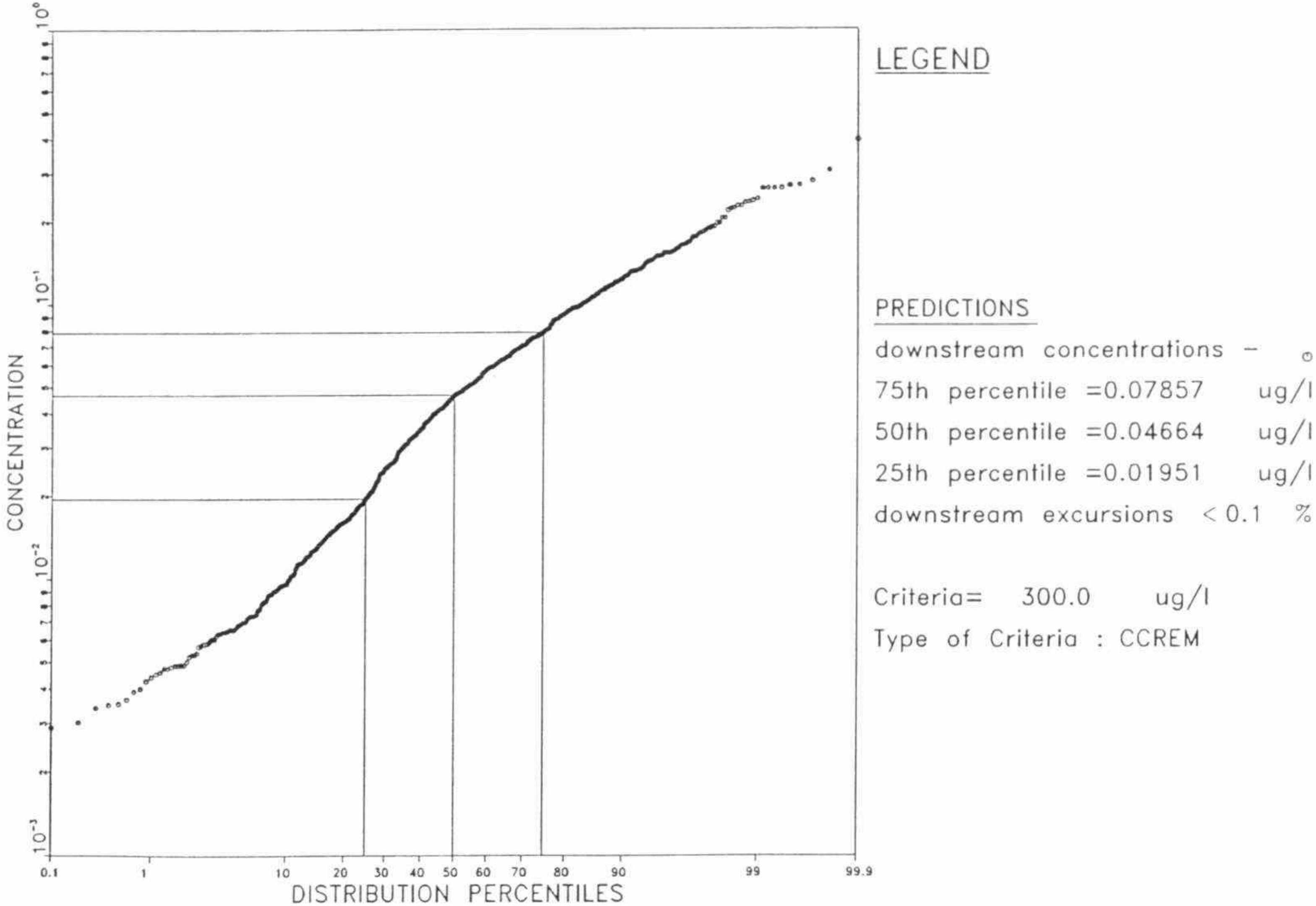
25th percentile =0.06015 ug/l

downstream excursions < 0.1 %

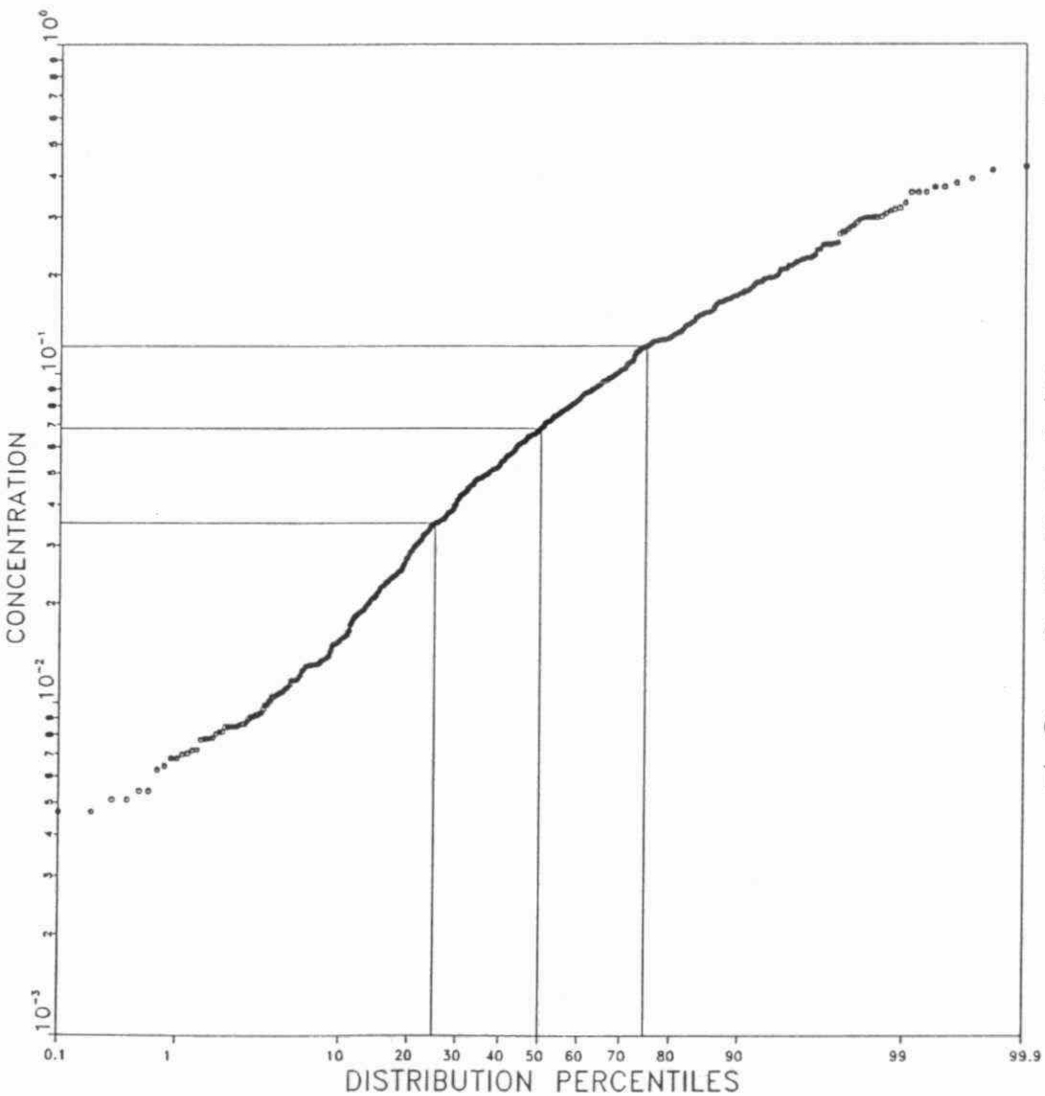
Criteria= 260.0 ug/l

Type of Criteria : CCREM

MONTE CARLO SIMULATION – TOLUENE



MONTE CARLO SIMULATION – TRICHLOROETHYLENE



LEGEND

PREDICTIONS

downstream concentrations – o

75th percentile =0.12114 ug/l

50th percentile =0.06828 ug/l

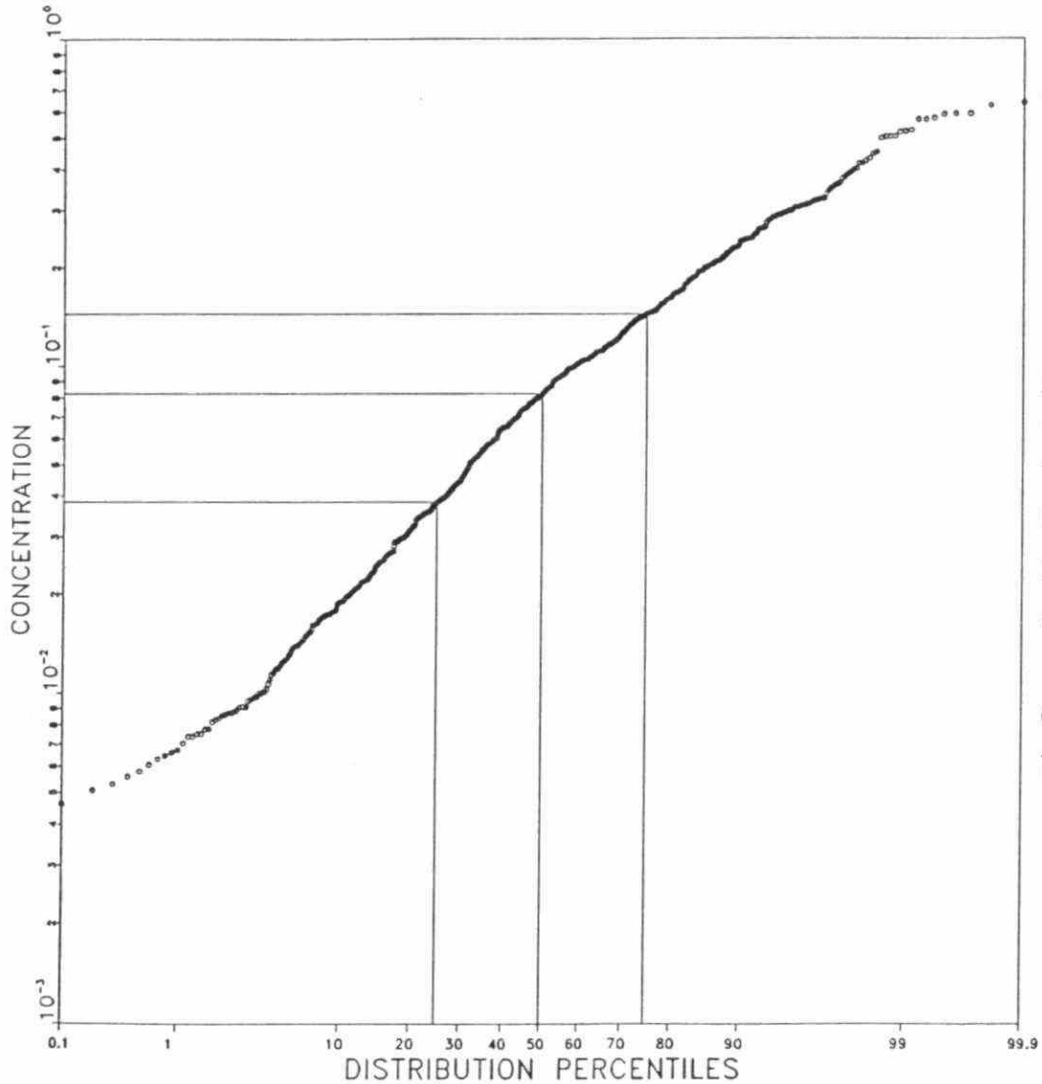
25th percentile =0.03514 ug/l

downstream excursions < 0.1 %

Criteria= 94.0 ug/l

Type of Criteria : MICHIGAN

MONTE CARLO SIMULATION – 1,1,1-TRICHLOROETHANE



LEGEND

PREDICTIONS

downstream concentrations – o

75th percentile =0.14467 ug/l

50th percentile =0.08235 ug/l

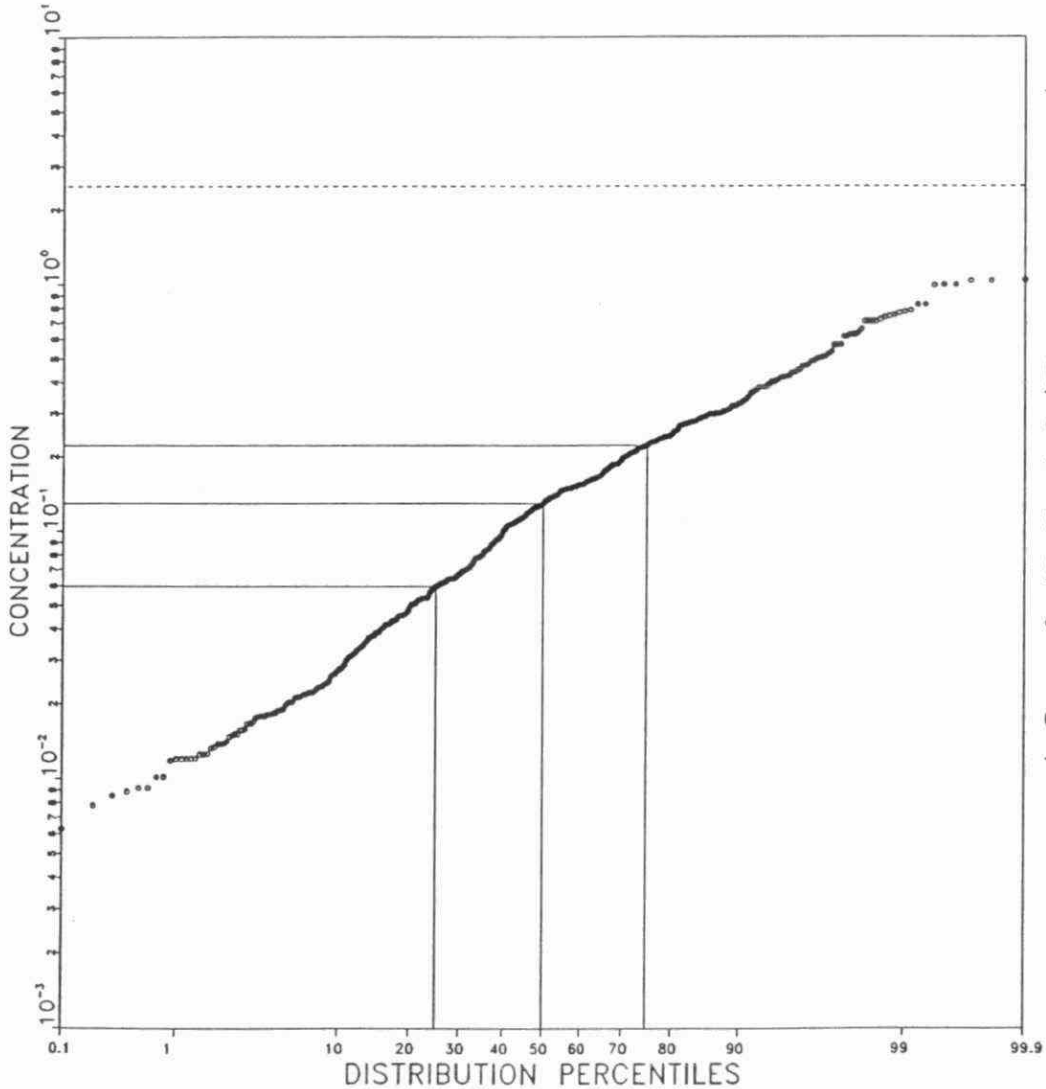
25th percentile =0.03842 ug/l

downstream excursions < 0.1 %

Criteria= 120.0 ug/l

Type of Criteria : CCREM

MONTE CARLO SIMULATION – 1,2 – DICHLOROBENZENE



LEGEND

PREDICTIONS

downstream concentrations – o

75th percentile =0.22237 ug/l

50th percentile =0.12972 ug/l

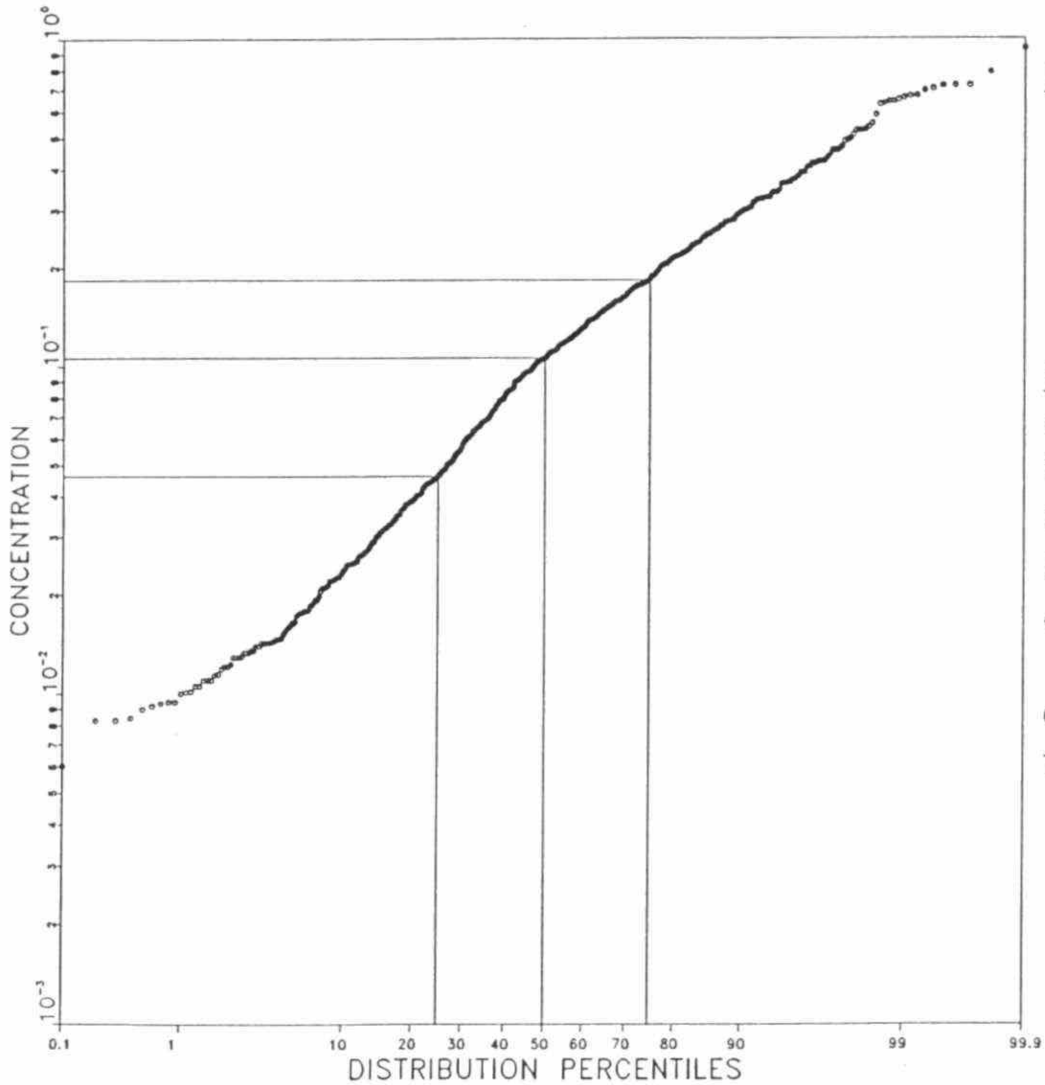
25th percentile =0.05985 ug/l

downstream excursions < 0.1 %

Criteria= 2.5 ug/l

Type of Criteria : PWQO

MONTE CARLO SIMULATION – 1,4 – DICHLOROBENZENE



LEGEND

PREDICTIONS

downstream concentrations – ⊙

75th percentile =0.18402 ug/l

50th percentile =0.10625 ug/l

25th percentile =0.04617 ug/l

downstream excursions < 0.1 %

Criteria= 4.0 ug/l

Type of Criteria : PWQO